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BUTTERWORTHS SCIENTIFIC PUBLICATIONS

Effect of Pressure on Turbulent Burning Velocity

B. FINE

Turbulent burning velocities were measured for three fuel–oxidant systems (propane–air, hydrogen–air, and propane–50 per cent oxygen–50 per cent nitrogen) over a range of pressures at nearly constant Reynolds number. At constant Reynolds number, the pressure exponent for turbulent burning velocity was consistently about 0·3 greater in magnitude than that for the corresponding laminar burning velocity. This result disagrees with usual concepts of turbulent combustion; the disagreement is probably due to inadequacy of the experimental method. Some observations on the effect of fuel concentration on the turbulent burning velocity of hydrogen–air flames are presented.

EARLY studies on turbulent burner flames at 1 atm pressure have established an empirical relation of the form[1]

$$S_T/S_L \propto R_e^{0.25} D^{0.26} \quad \ldots . [1]$$

where S_T/S_L is the ratio of turbulent to laminar burning velocity, D is the burner diameter in centimetres; and R_e is the Reynolds number for turbulent pipe flow, defined as

$$R_e = \bar{U} D \rho / \eta \quad \ldots . [2]$$

where, in turn, $\bar{U}$ is the mean stream velocity in cm/s, ρ is the density in g/cm^3 and η is the viscosity in poises. Since there is no appreciable variation of viscosity or density in these measurements, it is often questioned whether Reynolds number is a proper correlating parameter for turbulent burning velocity.

One purpose of the present work is to examine the validity of a Reynolds number relation by varying pressure. This is equivalent to varying density at constant initial temperature and molecular weight. A second purpose is to compare the observed pressure dependence with that predicted by various theories of turbulent flame propagation, in the hope of making some distinction among several models which have been proposed.

Since a flow system based on critical-flow orifices was used for metering fuel and oxidant, the mass flow into the flame zone was independent of the ambient burner pressure. This factor made it experimentally convenient to vary the burner pressure at constant Reynolds number since pressure changes would cause equal and opposite changes in density and gas velocity. The overall variation of Reynolds number among the several fuel–oxidant systems studied was not significant. The systems studied were propane–air, hydrogen–air, and propane burned with an oxidant mixture of 50 per cent nitrogen and 50 per cent oxygen by volume (henceforth referred to as 'propane–oxygen–nitrogen'). These were chosen so as to afford a large

range of laminar burning velocities and pressure exponents for laminar burning velocity.

APPARATUS AND PROCEDURE

Materials

Tank propane (CP grade) and tank hydrogen (98 to 99 per cent hydrogen) were used. The oxidants used were tank compressed air, water pumped, and a prepared oxygen–nitrogen mixture in the desired proportion. All gases were used without further purification.

Apparatus

The burner, flow system, and combustion chamber are described in detail elsewhere[2]. The cylindrical combustion chamber, 12 in. in diameter and 24 in. high, was fitted with two opposing rectangular glass windows. The combustion chamber led into a plenum which was connected to a vacuum pump that maintained reduced pressure in the chamber and exhausted combustion products. The pressure could be adjusted by a manual air bleed on the plenum and was read from a manometer connected to a pressure tap within the combustion chamber itself. The cylindrical burner was water-cooled near the lip and was about 125 cm long. Inserts of 1·016 and 1·89 cm diameter were used; thus, the length-to-diameter ratios were probably sufficient to ensure fully developed pipe turbulence. The burner was fitted into a round opening in the bottom of the combustion chamber by a pressure seal.

Experimental procedure

Incoming fuel and oxidant were metered separately through calibrated critical-flow orifices and then mixed. Ignition was effected at the burner port with a retractable spark igniter. The hydrogen–air and propane–oxygen–nitrogen flames were reactive enough to maintain boundary-layer stabilization over a reasonably large pressure range without the use of a pilot flame. An upper limit was imposed on the range of subatmospheric pressures available, because these reactive flames flashed-back while still below 1 atm. For the much less reactive propane–air flames, however, it was necessary to use a thin annular pilot flame of propane–air slightly enriched with oxygen, since unpiloted turbulent flames blew off even at 1 atm. For measurements with any single initial mixture, pressure was varied at constant mass flow and, therefore, constant Reynolds number. Among the three systems studied, the total range of Reynolds numbers covered lay between 3 000 and 6 300; this range is probably too small to involve any change in the nature of the turbulence.

Flames were photographed through the windows of the combustion chamber. For propane flames an exposure of about 0·5 second gave a suitable time-average image of the turbulent brush. For hydrogen–air flames which are much less luminous, an exposure of several seconds duration was required. The mean flame surface area A_f was obtained from measurements on negatives; its value was computed by lateral subdivision of

the flame image into two or three conical frusta. The turbulent burning velocity was then obtained by the relation

$$S_T = V / A_f \qquad \ldots . [3]$$

where the volume flow V was corrected to the ambient pressure in the chamber.

The mean flame surface was chosen as an approximation to the surface of maximum luminosity. As was pointed out by T. P. CLARK[3] and by J. HÜBNER and H. KLÄUKENS[4] the true surface of maximum luminosity is somewhat larger than the apparent, because the curvature of the turbulent brush displaces the apparent surface toward the burner axis. For several representative flames, therefore, an approximate correction based on the model treated in references 4 and 5 was applied to the mean flame surface. The correction increased values of S_T by about 5 per cent; since the correction was very nearly independent of pressure, the pressure exponents were unchanged. Because the correction is actually negligible, it has not been applied to values of S_T reported here.

RESULTS AND DISCUSSION

Data are shown in *Figures 1* to *3* inclusive plotted as $\log S_T$ against log pressure. For hydrogen–air flames, data were obtained at equivalence ratios* of 0·75, 1·10, 1·40, and 1·80 for which the total variation in Reynolds number was 3 100 to 4 500. Data for propane–oxygen–nitrogen flames were obtained at an equivalence ratio of 1 and a Reynolds number of 4 200. For these reactive flames a single burner 1·016 cm in diameter was used,

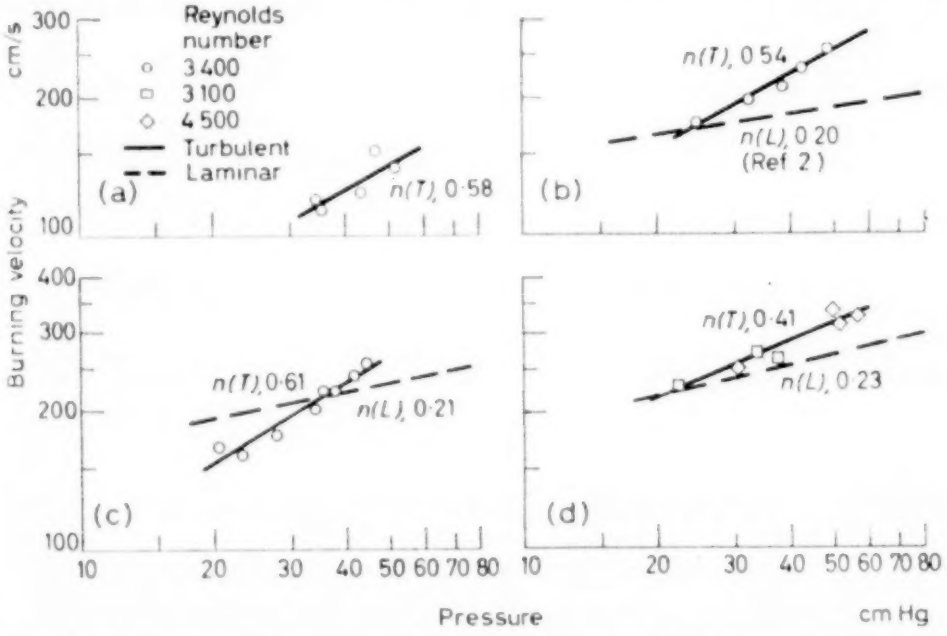

Figure 1. Burning velocities for hydrogen air flames. (a) *Equivalence ratio, 0·75;* (b) *equivalence ratio, 1·10;* (c) *equivalence ratio, 1·40;* (d) *equivalence ratio, 1·80*

*Equivalence ratio is defined as volumetric fuel/air ratio divided by volumetric fuel/air ratio for a stoichiometric mixture.

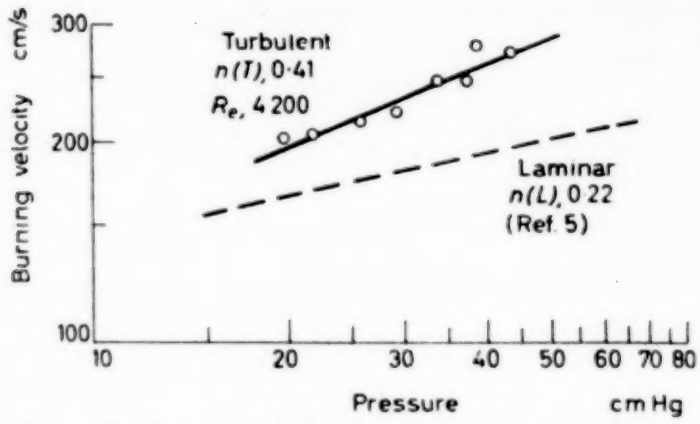

Figure 2. Burning velocity for propane–oxygen–nitrogen flames. Equivalence ratio, 1·00; percentage oxygen in oxidant, 50

since with any other available burners of significantly different diameter it was not possible to stabilize sufficiently luminous flames over a properly large pressure range. Data are shown for propane–air flames at equivalence ratios of 0·86 and 1·26 and for burners 1·016 and 1·89 cm in diameter. Reynolds number was constant for any given equivalence ratio and burner size, the overall range of Reynolds number lying between 3 000 and 6 300.

For turbulent hydrogen–air flames a pressure exponent of about 0·5 is found; for propane–oxygen–nitrogen, about 0·4. For propane–air flames S_T is very nearly independent of pressure; this independence was shown for

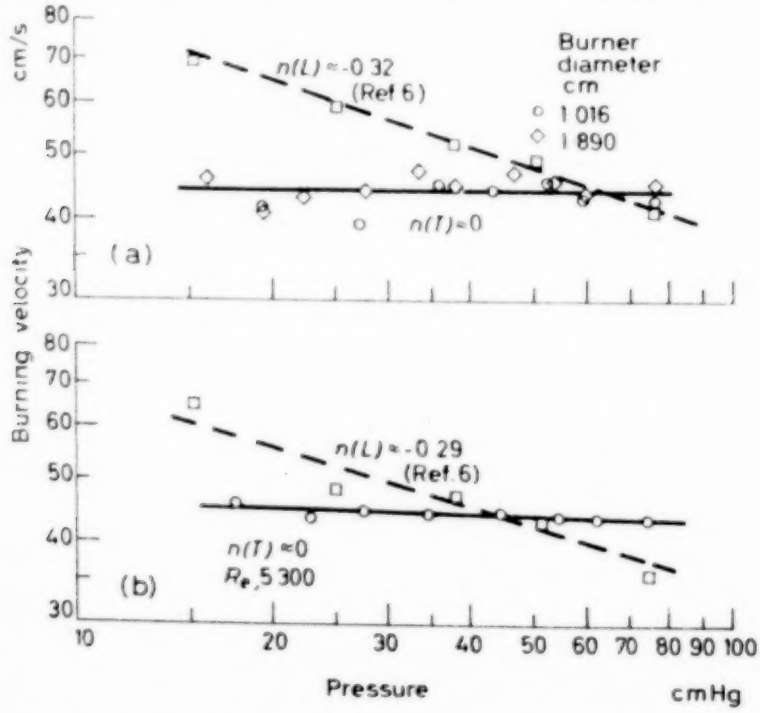

Figure 3. Burning velocities for propane–air flames. (a) Equivalence ratio, 0·86; (b) equivalence ratio, 1·26

both burners. Also shown in *Figures 1* to *3* are corresponding laminar burning velocities as a function of pressure. For hydrogen–air and propane–oxygen–nitrogen flames, these had been obtained by the total area of the schlieren cone[2, 5]. The same apparatus had been used for both turbulent and laminar burning velocities; the burner used for measuring S_T was one of several which had been used for measuring S_L.

The propane–air results[6], shown as upright squares in *Figure 3*, were cross-plotted from data of J. M. SINGER *et al.* These had been obtained from burner flames by a frustum method based on the visible cone. The pressure exponent, about $-0{\cdot}30$, is in good agreement with values reported by W. C. JOHNSTON and J. A. CYPHERS[7], $-0{\cdot}21$, and by R. E. CULLEN[8], $-0{\cdot}19$, also for burner flames. It agrees in sign and order of magnitude with the value reported by J. MANTON and B. B. MILLIKEN[9], $-0{\cdot}05$, based on pressure rise in a constant-volume bomb. The three exponents for propane–air based on burner flames had been obtained by both angle and area measurements. Since agreement among the three was felt to be satisfactory for present purposes, no redetermination was made.

It is seen that turbulent and laminar burning velocities for all three systems are correlated with pressure by a relation of the form

$$S_T / S_L \propto P^{[n(T)-n(L)]} \qquad \ldots . [4]$$

where $[n(T) - n(L)]$ equals about $0{\cdot}3$. Since S_L does not depend on Reynolds number, a dependence of S_T/S_L on pressure at constant Reynolds number indicates that S_T is not, in fact, a simple function of Reynolds number alone.

Results obtained by varying burner diameter (*Figure 3*) follow equation 1. In the present study, the burner size was varied at constant mass flow rate. Under these conditions equations 1 and 2 predict that S_T should be nearly independent of burner diameter, as is observed.

Relative values of S_T and S_L

The fact that $[n(T) - n(L)]$ has a value different from zero predicts that the laminar and turbulent lines will cross and that below some pressure S_L will actually exceed S_T. From *Figures 1* and *3*, it may be seen that this situation is found for hydrogen–air and propane–air flames. For propane–air data on the lean side the crossover pressure is about 1 atm; for rich data, crossing occurs at about 0·6 atm. For hydrogen–air flames the crossing occurs at 0·5 atm. In several cases, the amount by which S_L exceeds S_T, at a given pressure, is considerably larger than the probable uncertainty in S_T. For propane–oxygen–nitrogen flames, actual crossing was not observed within the measured pressure range, and the possibility still remains that these curves might have approached asymptotically without crossing. That S_L should exceed S_T is inconsistent with the concept that the effect of turbulence is to increase the rate of flame propagation. Even if one considers the fact that the scale of turbulence relative to the thickness of a laminar flame front changes with pressure, one cannot conclude that S_L should exceed S_T at any pressure.

Several explanations for the observed behaviour are suggested. First, the present experimental method may be inadequate as a measure of the rate of turbulent flame propagation. The large change in thickness over the various portions of the flame brush and corresponding changes in the nature of the combustion taking place make it quite possible that a measurement based on one simply defined surface through the flame brush does not give a correct pressure dependence of burning velocity. A second suggestion would be that measurement of S_T based on a single flame surface is adequate, but that the correct surface to use is the inner flame surface as originally suggested by G. DAMKÖHLER[10]. Such an inner flame surface might be analogous to the schlieren edge for laminar flames in representing the beginning of the reaction zone. A small amount of calculation for propane–air has shown that the inner flame surface gave the same independence of S_T with change of pressure, but a considerably higher value, about 72 cm/s, so that the laminar and turbulent curves would not cross in the measured range and the possibility of their approaching asymptotically would not be excluded. A third possibility is that the proper surface for measurement will change with pressure. K. WOHL[11], for example, has shown that the relative positions of the surfaces of maximum luminosity and 50 per cent oxygen consumption change with pressure for a low-pressure turbulent butane–air flame. If the proper surface for measurement moved toward the cold boundary with decreasing pressure, this would tend to increase S_T at lower pressures and, perhaps, would eliminate the crossing of the curves. Such a procedure would imply that, when the surface of measurement reached the cold boundary, the flame would have the properties of a thickened laminar reaction zone. The fact that the observed crossover pressures are widely different for different flames would imply that the behaviour of the surface would be different for each flame. At present, however, there is no way of deciding how the surface of measurement should vary with pressure, except perhaps by assuming initially that S_T and S_L should have the same pressure dependence.

Comparison with theory

The most widely considered concept of turbulent flame propagation states that, if the scale of turbulence is large compared to the thickness of a corresponding laminar flame, the effect of turbulence will be to wrinkle the laminar flame front so as to produce a brush. In most theoretical treatments, the usual procedure is to assume a geometry of flame wrinkling and derive expressions for S_T/S_L based primarily on that geometry, modified perhaps by consideration of such factors as the statistical nature of turbulence and the steady effect of flame propagation. When it is assumed that the velocity with which an eddy is swept across the flame front is S_L or S_T, these lead to expressions of the form[12]

$$S_T/S_L = f(u'/S_L) \qquad \ldots . [5]$$

where u' is the magnitude of the longitudinal turbulent velocity fluctuation. The pressure dependence of S_T/S_L will depend, therefore, on the pressure dependence of u'/S_L. According to the statistical theory of isotropic turbulence, the equations describing the dissipation of kinetic energy into

turbulence do not involve the density, so that the relative intensity of turbulence u'/U should be, at least to a first approximation, independent of pressure at constant Reynolds number, and the actual fluctuation u' should vary approximately as P^{-1}. Since the pressure dependence of S_L has always been observed to be plus or minus a few tenths, the pressure exponent of S_T/S_L will be negative and, actually, the pressure dependence of S_T/S_L will be negative. This is just opposite to what is observed experimentally.

A second theory has recently been proposed[13] which asserts that the effect of turbulence on flame propagation is to thicken the reaction zone and that the turbulent brush is merely an extended laminar flame. This concept leads, on the basis of a thermal mechanism, to the following expression for S_T/S_L

$$\frac{S_T}{S_L} = \left(\frac{k + k'}{k}\right)\frac{D_L}{D_T} \qquad \ldots . [6]$$

where D_L/D_T is the ratio of laminar to turbulent flame thickness; k, the thermal conductivity; and k', the eddy conductivity. The first term in equation 6 can be written as $(1 + zR_e)$ where z is some constant and is therefore independent of pressure at constant Reynolds number. The quantity D_L has generally been observed to vary inversely with pressure. Furthermore, measurements on photographs of flame studies in the present work showed that the thickness of the turbulent brush D_T, defined either as the difference in heights of the inner and outer cones or as the width of the brush at the top of the inner cone, did not change if pressure was reduced at constant Reynolds number. Thus, the extended reaction zone theory predicts the same negative pressure dependence as was predicted on the basis of flame wrinkling at least with flames for which D_T is independent of pressure. It does allow, however, that S_L should exceed S_T at some pressure, in contrast to wrinkled flame theories.

It appears, then, that measurements of turbulent burning velocity based on measurement of a fixed surface through the bunsen cone give results which cannot be explained in terms of present theory. Both theory and experiment are probably inadequate for treating the effect of pressure on turbulent burning velocity.

Turbulent burning velocity of hydrogen–air flames at constant pressure

It has generally been observed that the burning velocity for laminar hydrogen–air flames attains its peak value at a much richer hydrogen concentration than would correspond to the stoichiometric concentration of about 29 per cent. It was therefore of interest to observe whether turbulent hydrogen–air flames would show a different behaviour. *Figure 4* shows laminar[2] and turbulent burning velocities as a function of volume percentage of hydrogen for a pressure of 0·61 atm. It is seen that the peak concentration for S_T has not been reached; it is apparent, however, that S_T will not reach a maximum significantly closer to a stoichiometric concentration than does S_L. One significant difference may be noted, however, between the behaviour of laminar and turbulent hydrogen–air flames. It has often been reported that lean or stoichiometric, laminar, hydrogen–air flames show open tips

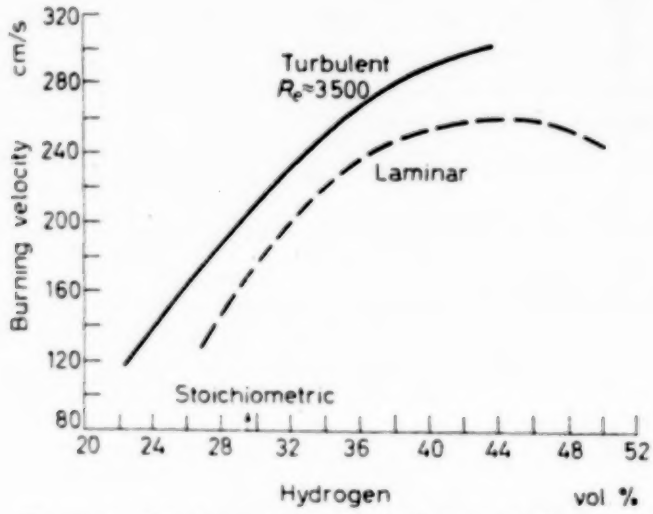

Figure 4. Burning velocity for hydrogen–air flames at pressure of 0·61 atm

and a shape which is polyhedral and often unsteady. This effect has generally been attributed[11] to preferential diffusion of hydrogen out of the region of the flame tip. It is observed, however, that the lean turbulent hydrogen–air flames shows a perfectly normal flame brush and that turbulent burning velocities at an equivalence ratio of 0·75 (as lean as measurable images could be obtained) lay on the same curve as those obtained at higher concentrations of hydrogen.

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Lewis Flight Propulsion Laboratory,
Cleveland, Ohio

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Separation of the Products of Cool Flame Oxidation of Propane

C. R. YOKLEY and R. E. FERGUSON

The techniques of gas chromatography and low temperature, low pressure distillation have been applied to the problem of the separation and isolation of the major products of cool flame oxidation of propane. The methods described are adequate for separating and handling the reaction products in small amounts without appreciable contamination. Data on column performance are presented.

THE techniques of gas chromatography and low temperature, low pressure distillation have been successfully applied to the problem of the separation and isolation of most of the major products of the cool flame reaction in propane–oxygen mixtures. The product mixtures dealt with are typical of those encountered in investigations of slow oxidation in the gas phase. For this reason the methods used are reported in some detail in the hope that they can be easily put to use by those working on similar problems.

Our primary interest in this work was to develop means of isolating the major products of cool flame oxidation of propane-2-^{13}C. Such separation is necessary before reliable isotope analyses of the products can be obtained by mass spectrometry. Others have in the past contemplated oxidation studies using ^{13}C-labelled propane, but adequate separation techniques were not then available and the experiments were considered impracticable[1].

The main difficulties in work of this kind result from the small sample size and the diversity of the products. In our experiments, for example, 33 cm^3 (n.t.p.) of propane were allowed to undergo reaction. Roughly a third of the original material decomposed, giving rise to eighteen definitely identified products, some of which were present in amounts less than 0.1 cm^3 (n.t.p.) of gas. The resolution of these mixtures presents a problem to which gas chromatography is uniquely applicable. The methods to be described, using this technique, were adequate for separating and handling the major reaction products without appreciable contamination and usually with negligible loss.

All preliminary work on separation, the subject of this paper, was done with cool flame reaction products of ordinary propane in amounts comparable to those expected in later experiments with propane-2-^{13}C (the results of the latter study will be published in another report). Since the interest in this work was on the origin of products, no concerted attempt was made to achieve overall quantitative results.

NATURE OF THE PROBLEM

Table 1 shows an estimate of the major products, positively identified, found in a typical cool flame product mixture.

Table 1. Products identified in cool flame oxidation of propane; 66 cm³ (n.t.p.) of an equimolar mixture of propane and oxygen taken initially

Non-condensable gases separated on Column I		*Volatile at −140°C separated on Column II*		*Remaining products separated on Column III*	
Component	*cm³ (n.t.p.) gas*	*Component*	*cm³ (n.t.p.) gas*	*Component*	*cm³ (n.t.p.) gas*
Hydrogen	*	*Ethane*	0·1	*Ethylene oxide*	0·1
Oxygen	*	*Ethylene*	0·6	*Acetaldehyde*	1·3
Carbon monoxide	1·0	*Carbon dioxide*	3·0	*Propylene oxide*	0·4
Methane	0·1	*Propane*	24·0	*Acetone*	0·4
		Propylene	1·7	*Propionaldehyde*	0·03
				Methanol	7·0
		Formaldehyde	>0·3†	*Ethanol*	0·1
				2-Propanol	0·1
				1-Propanol	0·02
				Water	*

*Not measured.
†Not separated by gas chromatography. See text.

The reaction in this case took place in an equimolar mixture of propane and oxygen in a Vycor bulb at 318°C, 421 mm of mercury, after an induction period of 52 seconds, and consisted of a series of six pressure pulses after which reaction sensibly ceased. About 30 per cent of the propane was decomposed. The conditions will not be characterized further since the emphasis here is on the product mixture itself. We have observed, however, that the extent of reaction and also the major product distribution change little with variations of initial temperature and pressure within the cool flame (pressure pulse) region.

The data in *Table 1* were obtained from gas chromatograms or pressure/volume measurements on isolated components, except in the case of formaldehyde, and should be considered approximate. Analyses of total product mixtures by mass spectrometry roughly confirm these data. The amount of formaldehyde listed is that recovered by an inefficient method to be described later; it represents merely a minimum value.

Separated products were identified initially by both mass spectrometry and gas chromatography; after this the latter technique alone could be used with confidence for identification by elution time.

Considering the nature of the product mixture, it is obvious that more than one type of column must be used for final separation, and that a preliminary separation into groups, each group conveniently resolvable on an appropriate column, is necessary. This might be done by gas chromatography, but in this work low temperature distillation was chosen for the purpose for the following reasons:

(*1*) All or most of the formaldehyde was lost on all columns tried.

(*2*) For convenience in handling, the condensable products were collected initially at liquid nitrogen temperature. The resulting solid undoubtedly contains reactive materials such as peroxides, and during repeated melting and vaporization incident to chromatographic separation, there is the

possibility of secondary reactions and polymerization of some components. Preliminary separation at low temperature reduces the risk for the more volatile fractions.

(3) This method allows separation of portions of the aldehydes and methanol from water. With water present, confusing chromatograms (complex unresolved peaks containing aldehydes, alcohols and water) were sometimes obtained. Slow vaporization of water-containing fractions from the unheated inlet trap may have been partially responsible for the overlapping. In any case, there was no trouble of this sort with water absent.

The procedure finally selected was separation by volatility into five fractions and subsequent resolution of each of these on an appropriate one of three columns. A. B. CALLEAR and R. J. CVETANOVIC[2] have also employed preliminary low temperature distillation to advantage in the analysis of oxidation product mixtures.

APPARATUS

The apparatus, consisting of a reaction bulb and manometer, gas handling system, low temperature still, and gas chromatography line, was constructed for convenience as one integral vacuum system.

Low temperature still

The low temperature still was similar to that described by D. J. LEROY[3]; it is used in much the same way as an ordinary cold trap for fractionation on the vacuum line, but it has the advantage of continuously variable temperature which is easily controlled. Copper–constantan thermocouples and an indicating potentiometer were used to follow the still temperature; they were calibrated as a unit over the range of interest (-190°C to -40°C) by comparison of a series of vapour pressure measurements on carbon dioxide, 2-methyl butene-1 and 2-methyl propane with those reported in the literature. Temperatures given are probably accurate to $\pm 3^{\circ}$C. The pressure during distillation was monitored by recording the output of a thermocouple vacuum gauge open to the distillation line. The gauge was calibrated only for air, since it was used mainly for determining the end of a distillation, signified by a drop in pressure, say from a few tenths of a millimetre of mercury, a typical dynamic distillation pressure, to a few microns of mercury. A paper by LeRoy describes operation of the still in detail[3].

Gas chromatography line

This system is shown schematically in *Figure 1*(a). It was constructed of glass, with interconnections in the line itself of 2 mm bore capillary tubing, and with larger bore connections from input and output traps to other parts of the vacuum system. The latter arrangement allowed vacuum manipulation of mixture and convenient recycling of components through the column.

The helium carrier gas was purified by passing it through an activated charcoal trap at liquid nitrogen temperature. Flow was measured by float

type glass flowmeters; flow through the column was controlled by settin the tank regulator pressure, and that through the reference thermal co ductivity cell was adjusted by a needle valve. A 500 cm³ surge volum manostat and vacuum pump maintained a constant pressure of abo 100 mm of mercury at the low pressure end of the line. Low downstrea pressures were used to obtain a high pressure ratio across the colum without the necessity of high input pressure, which was limited because the use of glass stopcocks in the inlet system. During operation the colum were immersed in temperature-controlled oil or water baths in Dewar flask

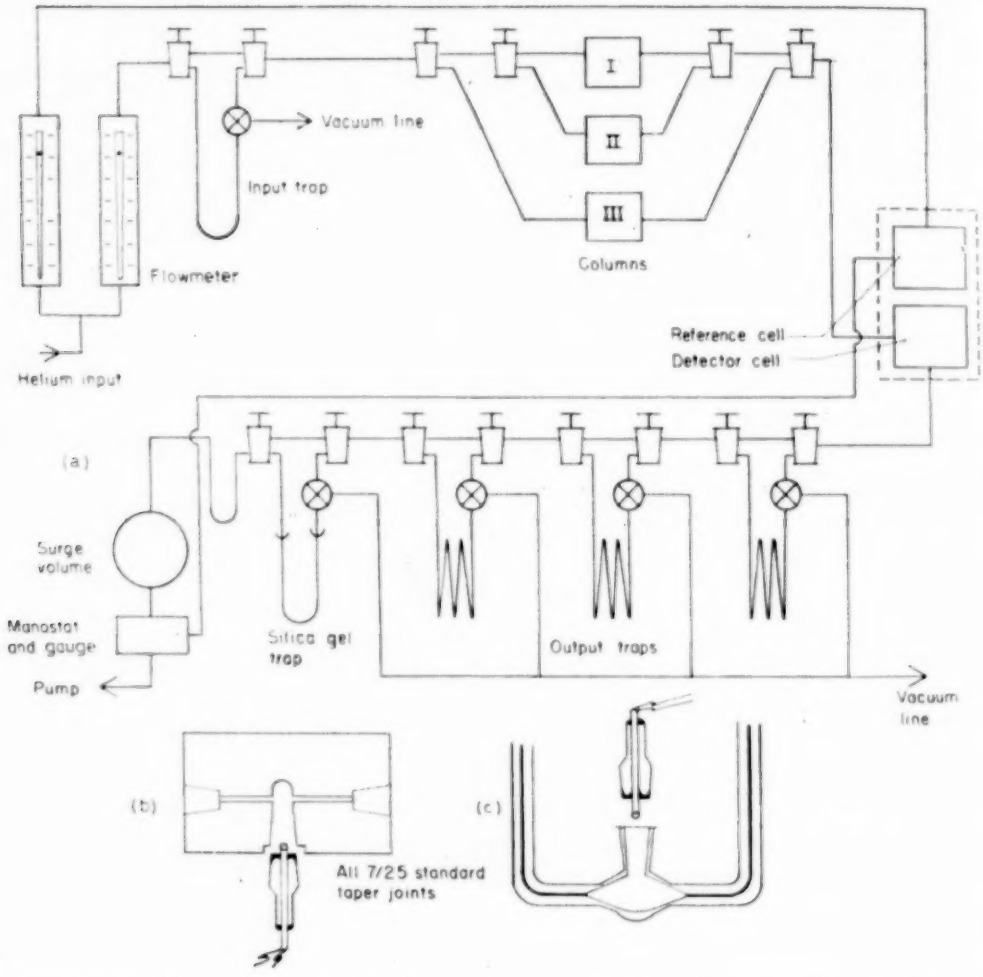

Figure 1 (a). *Gas chromatography line used for separation and isolation of cool flame products;* (b). *Brass thermistor detector cell;* (c). *Glass thermistor detector cell.*

Detector cells—The thermistor type thermal conductivity cells were of simple design. Glass covered probe type thermistor beads (Thermistor Corporation of America, Code 32PB1) were cemented into inner 7/25 standard taper glass joints with an epoxy resin (Shell Epon Resin 828) as shown in *Figure 1*(b), and inserted into a standard socket in a brass block through which the carrier gas passed. The joints were made tight with

stopcock grease or vacuum wax. Subsequent experience has shown that a very simple all-glass cell, as shown in *Figure 1*(c), is adequate for most work. The thermistor cells were immersed in a mercury bath in a Dewar flask without further temperature control, and were connected in the usual way in an equal-arm Wheatstone bridge circuit (all resistances approximately 2000 ohms) with 6 to 12 V storage battery supply. The bridge output was connected through a simple voltage divider attenuator to the input circuit of a 1 mV Speedomax recorder.

To enable comparison of this detector [*Figure 1*(b)] with others, a determination of sensitivity apart from connection with the column was made. With helium passing through the reference cell and a mixture of 0·293 mole per cent of propane in helium passing through the measuring cell at 24° C, the bridge unbalance at the output terminals and across a 2500 ohm parallel attentuator was 4·58 mV. This reduces to a sensitivity of 15·6 mV per 1 per cent diluent in the carrier gas. The determination was made at 100 mm of mercury, a flow rate of 70 cm^3 (n.t.p.)/min, and with a controlled bridge current of 6·1 mA.

The sensitivity and base line stability of the apparatus were such that 1 microlitre (n.t.p.) (vapour) of compounds boiling below 70° C could be detected under the conditions employed in this study. Substances with higher boiling points, having greater elution times, required more sample because of peak broadening; to give a specific example, 14 microlitres (n.t.p.) of ethanol vapour, eluted in 16 minutes, gave a 6 mm pen deflection at full sensitivity. A 1 mm deflection was sufficient for detection.

Traps—The input and output traps were made from two high-vacuum grade parallel oblique bore three-way stopcocks and a T-bore stopcock for connection to the vacuum line, as shown in *Figure 1*. The first three collecting traps, used for condensable gases, were triple U traps of 4 mm standard wall tubing. The loops were half submerged in liquid nitrogen and under these conditions 99 per cent or more of the condensable components was recovered. A single U trap was only about 67 per cent efficient at the highest carrier gas flow rates used, 75 cm^3 (n.t.p.)/min at 100 mm of mercury pressure downstream from the column. The fourth trap, containing a small plug of 60 mesh silica gel degassed by flaming and pumping, was used for recovery of carbon monoxide and methane at liquid nitrogen temperature. Hydrogen and helium were not appreciably absorbed and could be removed by pumping.

The traps were used in the obvious way: the carrier gas was bypassed until the desired elution peak appeared, the stopcocks were turned so as to divert the flow through the trap, and the trap was closed off again at the end of the peak. Between each use the traps were pumped out and thoroughly flushed with the carrier gas.

Gas chromatographic columns—Three columns were used for resolution of the fractions separated by volatility: a charcoal adsorption column for non-condensable gases, a silica gel column for hydrocarbons and carbon dioxide, and a gas–liquid partition column with bis[2-(2-methoxyethoxyl)ethyl] ether as the liquid phase for separation of oxygenated compounds. The

latter was selected after many trials of various liquids, including the usual diffusion pump oils, silicone oils, ethylene carbonate, and glycerol; it was the only solvent of those tried which, with proper selection of column temperature, could be used to separate all the major oxygen-containing compounds, except formaldehyde, on a single column.

Column specifications and some details to indicate performance are given in the following paragraphs.

Column I was a 13 ft helix of $\frac{3}{16}$ in. o.d., 0·118 in. i.d. stainless steel tubing packed before winding with 50 mesh coconut charcoal. With inlet and outlet pressures of 1 500 mm and 100 mm of mercury, the helium flow through the column was 7·5 cm³/min at 24°C. The efficiency, checked using a carbon monoxide elution peak in accordance with the procedure recommended by D. H. DESTY and others[4], was 784 theoretical plates at 24°C.

Column II was a 6·5 ft, $\frac{1}{4}$ in. o.d., 0·18 in. i.d. stainless steel tube packed with 40 to 60 mesh silica gel and bent to form a multiple **U** column. The helium flow rate was 26 cm³ (n.t.p.)/min with inlet and outlet pressures of 782 mm and 120 mm of mercury at 61°C. At this temperature the efficiency was found to be 580 theoretical plates using measurements on a propylene elution peak.

Column III was a gas–liquid column of 40 to 60 mesh C-22 firebrick carrying 30 per cent by weight of bis[2-(2-methoxyethoxy)ethyl] ether packed into an 8·3 ft multiple **U** tube of 4·5 mm i.d. Pyrex. With inlet and outlet pressures of 1 480 mm and 110 mm of mercury, the helium flow rate was 47 cm³ (n.t.p.)/min at 49°C. Three measurements of efficiency were made: at 49°C it was 565 theoretical plates (acetaldehyde peak); at 19°C, 1 166 theoretical plates (propylene oxide peak); and at 3°C, 1 230 theoretical plates (acetaldehyde elution peak).

PROCEDURE

Tables 1 and *2* together outline the overall separation procedure. *Table 1* shows the three main groups of products obtained by distillation and indicates the column used for further separation. *Table 2* gives more information on the fractions separated on Column III. The details were as follows.

At the end of the cool flame reaction the products were expanded slowly through a triple **U** trap at liquid nitrogen temperature into a side-arm containing 0·3 g of degassed silica gel cooled by liquid nitrogen. Non-condensable gases excepting hydrogen were absorbed on the silica gel, where they were stored, and the other products were caught in the cold trap. The condensable material was then distilled rapidly to the LeRoy Ward still at −196°C and kept at this temperature, with the still closed until the components of the non-condensable mixture were separated.

Non-condensable gases

A portion of the non-condensable fraction was transferred by expansion to the input trap on the chromatography line and the carbon monoxide and methane were separated on the charcoal column at 24°C [helium flow 7·5 cm³ (n.t.p.)/min]. There was sufficient time between the carbon monoxide and methane peaks to collect and transfer them separately using the one available silica gel output trap. The pure samples were transferred, after pumping the helium away at liquid nitrogen temperature, by readsorption to sample tubes containing silica gel at −196°C.

Hydrocarbons and carbon dioxide

The next fraction, containing hydrocarbons, carbon dioxide, and some of the formaldehyde, was transferred from the still at −140°C (dynamic pressure *ca.* 0·9 micron of mercury) to a side-arm at −196°C. This distillation required about 20 minutes because of the large excess of propane in this fraction; the end was indicated by a sudden pressure drop when the propane was gone. The pressure did not go to zero since formaldehyde, probably trapped in ice in the still, continued to come off at a very slow rate. Only a fraction of the total formaldehyde could be recovered during this operation, but the 0·25 to 1 cm^3 obtained up to the end of the propane distillation was enough for isotopic analysis. The hydrocarbons were removed except for a small trace of propane.

For partial recovery of formaldehyde, the fraction volatile at −140°C was distilled into a bulb at −196°C containing 5 cm^3 of degassed distilled water. The bulb was warmed and shaken to dissolve formaldehyde, the contents were refrozen and pumped at −196°C, and the hydrocarbons and carbon dioxide were distilled off quickly at −80°C. The solution, containing most of the formaldehyde recovered from the still, was set aside for later treatment.

Hydrocarbons and carbon dioxide were separated on the silica gel column at 61°C [helium flow 26 cm^3 (n.t.p.)/min]. A tracing of a typical chromatogram is shown in *Figure 2*(a). All peaks were well resolved and the purity of the separated components was greater than 99·9 mole per cent in all cases as determined by mass spectrometry. Traces of water from the silica gel column (very difficult to remove) were eliminated by distilling components from the output traps at −80°C. Occasionally some components from this separation and also from subsequent still fractions were recycled through the column to ensure purity of the compound.

Formaldehyde

The formaldehyde in water solution was oxidized to formate and then decomposed to carbon monoxide by the following procedure. A suspension of 1 millimole of freshly precipitated silver oxide in 2 cm^3 of a solution containing 1 millimole of sodium hydroxide was added to the formaldehyde solution. The mixture was boiled and the silver oxide was separated from the hot solution by centrifuging. The clear solution containing sodium formate was partially neutralized (pH 8) with sulphuric acid and evaporated to dryness in a small flask which could be attached to a dropping funnel assembly on the vacuum line. After degassing, the solid was decomposed *in vacuo* with degassed concentrated sulphuric acid and the gaseous products were adsorbed on silica gel at −196°C. The carbon monoxide produced was separated from small amounts of air and carbon dioxide by gas chromatography using the charcoal adsorption column (Column I).

The entire purpose of this method was to obtain the carbon from formaldehyde in a form suitable for isotopic analysis by mass spectrometry. In trials using commercial formalin solution the yields of carbon monoxide were usually greater than 85 per cent. Other methods tried and rejected included catalytic hydrogenation to methanol followed by purification

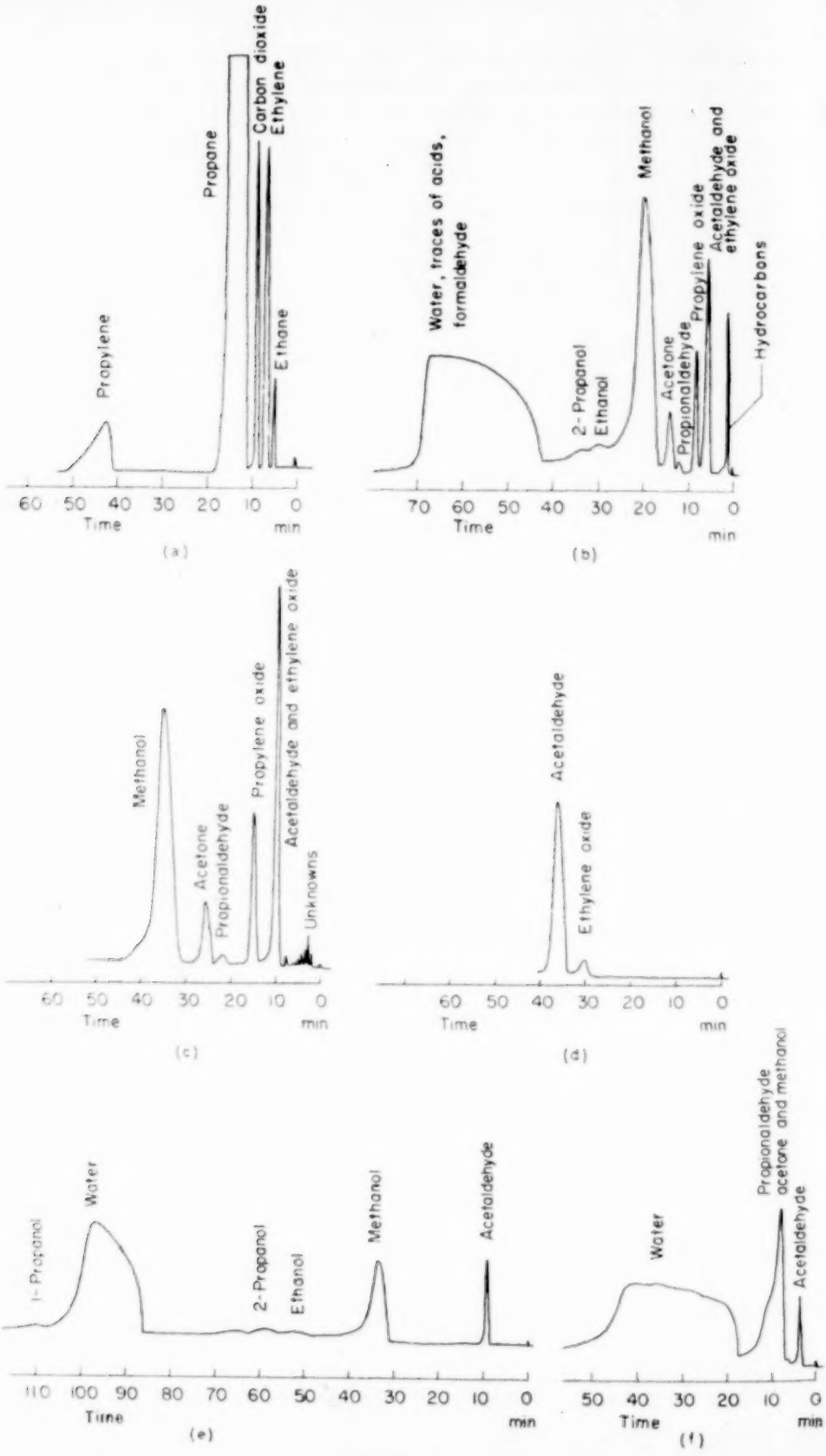
Propylene
Propane
Carbon dioxide
Ethylene
Ethane
60 50 40 30 20 10 0
Time
min
(a)
Water, traces of acids, formaldehyde
2-Propanol
Ethanol
Methanol
Acetone
Propionaldehyde
Propylene oxide
Acetaldehyde and ethylene oxide
Hydrocarbons
70 60 50 40 30 20 10 0
Time
min
(b)
Methanol
Acetone
Propionaldehyde
Propylene oxide
Acetaldehyde and ethylene oxide
Unknowns
60 50 40 30 20 10 0
Time
min
(c)
Acetaldehyde
Ethylene oxide
60 50 40 30 20 10 0
Time
min
(d)
1-Propanol
Water
2-Propanol
Ethanol
Methanol
Acetaldehyde
110 100 90 80 70 60 50 40 30 20 10 0
Time
min
(e)
Water
Propionaldehyde acetone and methanol
Acetaldehyde
50 40 30 20 10 0
Time
min
(f)

Figure 2

by gas chromatography of the methanol (very low yields, side reactions), combustion of the bisulphite addition product to give carbon dioxide (possible interference by acetaldehyde), and separation of formaldehyde itself on a silicone oil gas–liquid partition column (simply unsuccessful).

The remaining products

The material remaining in the LeRoy–Ward still after the preceding distillation was separated by three more distillations, at −60°, −40°, and 25°C. These three distillations served the purpose, mentioned above, of removing some of the oxygen-containing compounds from reactive species and water at low temperature. The results are shown in *Table 2*.

Table 2. Results of low-temperature distillation of products condensable at −140°C. Each fraction was separable on Column III

Component	*Estimated composition of still fractions cm³ (n.t.p.) gas*		
	−60°C	*−40°C*	*Volatile at 25°C*
Ethylene oxide	0·1		
Acetaldehyde	0·9	0·3	0·04
Propylene oxide	0·4		
Propionaldehyde	0·03		
Acetone	0·2		
Methanol	4·02	1·65	1·2
Ethanol		0·07	0·06
2-Propanol		0·08	0·03
1-Propanol		0·02	
Water		*Not measured*	*Not measured*

The temperatures for distillation were chosen by repeated trials followed by gas chromatographic analyses of the fraction taken. The separations were not clean; commonly the dynamic pressure decreased slowly during the recovery of a fraction at constant temperature. A distillation was terminated at some pressure, ordinarily a few microns of mercury, found by experience to give a convenient cut. The procedure finally selected would not be convenient for routine quantitative work. It was the best way found, however, to clean up the chromatograms and enable detection and recovery in pure form of some of the components such as ethyl- and propyl-alcohols.

Figure 2(b) illustrates the problem. This is a chromatogram of the entire product mixture after removal of non-condensables and some of the

Figure 2. Tracing of typical gas chromatograms obtained in the separation of cool flame products of propane. (a). *Hydrocarbon fraction; Column I (silica gel) at 61°C, helium flow 26 cm³ (n.t.p.)/min;* (b). *Total cool flame products after partial removal of hydrocarbons and formaldehyde; short (5 ft) column with bis[2-(methoxyethoxy)-ethyl] ether as liquid phase at 50°C, helium flow 75 cm³ (n.t.p.)/min;* (c). *Low temperature still fraction volatile at −60°C; Column III, temperature 49°C, helium flow 33 cm³ (n.t.p.)/min;* (d). *Separation of acetaldehyde and ethylene oxide peak shown on Figure 2*(c)*; recycled on the same column at 3°C, helium flow 39 cm³ (n.t.p.)/min;* (e). *Still fraction taken at −40°C; Column III at 41·5°C, helium flow 20 cm³ (n.t.p.)/min;* (f). *Room temperature still fraction; Column III at 99·2°C, helium flow 10 cm³ (n.t.p.)/min*

hydrocarbon fraction, obtained with a short (5 ft) bis[2-(methoxyethoxy)-ethyl] ether column at 50°C [helium flow 75 cm^3 (n.t.p.)/min]. Complete resolution of components eluted before methanol can be achieved by lowering the column temperature. However, this causes the large methanol peak to trail out and to overlap components eluted later. Preliminary low-temperature distillation, in addition to having the advantages already described, serves to reduce the amount of methanol in the still fractions containing the higher alcohols, and thus enables clear separation of methanol from the components coming after.

Distillation at −60°C resulted in a fraction easily resolved on Column III at 49°C [helium flow 33 cm^3 (n.t.p.)/min], *Figure 2*(c), except for acetaldehyde and ethylene oxide, which are eluted together at this temperature. The mixture giving rise to this peak was recycled through the column at 3°C [helium flow rate 39 cm^3 (n.t.p.)/min] to separate the two components, as shown in *Figure 2*(d). Over half the methanol was recovered from the product mixture at −60°C. That remaining was probably trapped in ice in the still; the same is true of some of the acetaldehyde.

The fraction taken at −40°C contained some water and 1·6 cm^3 of methanol, not enough to interfere with the separation of ethyl and propyl alcohols from this still fraction. The separation was made on Column III at 41·5°C [helium flow rate 20 cm^3 (n.t.p.)/min] and is illustrated in *Figure 2*(e).

The last fraction, volatile at room temperature, contained mostly water along with some lower-boiling products left over presumably because of entrapment in ice. The water peak [*Figure 2*(f)] contained methanol and acids in trace amounts, some formaldehyde, and probably traces of components remaining undetected. Polymerized material, chiefly formaldehyde, remained in the still at the end of the procedure.

DISCUSSION

Purity of the separated products

Mass spectrometric analyses of isolated samples have shown purities usually in the range 99·9 per cent for the smallest samples, *ca.* 0·1 cm^3 (n.t.p.). The impurities reported were in very few cases components of adjacent elution peaks, indicating that resolution is, in fact, about what one would expect from the chromatograms and that in difficult cases, traces of impurities from adjacent peaks can be easily eliminated by trapping the major portion of a peak and rejecting the leading and trailing portions, or by recycling the compound through the same column operated at a higher efficiency.

A rather ubiquitous impurity in this study was formaldehyde. Recent work has indicated that some formaldehyde does get through a bis[2-(2-methoxyethoxy)ethyl] ether column. It appears as a wide peak of very low maximum concentration which, on *Figure 2*(b), would spread from the acetaldehyde peak through the methanol peak and in trace amounts on through the chromatogram. If formaldehyde is allowed to get into the column input, samples trapped from the region mentioned will contain

formaldehyde as a trace impurity. Because of its low concentration in the carrier gas stream and because of its tendency to polymerize on standing there was not enough present in samples of other products to interfere with isotopic analyses.

Another trace impurity was an unidentified compound of molecular weight 104. It was present in trapped samples with elution times greater than that for acetone. The methanol peak shown in *Figure 2*(e) contained 0·1 mole per cent of this compound. The acetaldehyde and propylene oxide peaks from the second low temperature distillation at −60° C showed unidentified mass peaks up to 86 but the impurities amounted to less than 0·1 per cent of the main components.

Some difficulty was experienced in the use of adsorption on cold silica gel for vacuum handling of small amounts of non-condensable gases. It is difficult to degas silica gel by prolonged flaming and pumping; adsorption and desorption of carbon monoxide on apparently degassed gel, for example, results in the contamination of the sample with air. This was usually so slight as to be negligible, but it invariably occurred. The use of activated charcoal may be preferable[5].

Adaptability of the methods for quantitative analysis

The procedure outlined above suffices for quantitative analysis of non-condensable gases, hydrocarbons and carbon dioxide. Modifications would be desirable for the determination of the remaining species because the distillation scheme used here would be awkward. A one-stage analysis [*Figure 2*(b)] of the oxygenated product mixture would seem practicable if a heated inlet system and detector cell were used for rapid introduction of the sample and to prevent condensation of water in the detector. There is of course the risk of loss of reactive species in such a procedure. Another possibility is the use of column temperature programming as employed by C. M. Drew and J. R. McNesby[3] to sharpen the elution peaks in the methanol region of the chromatogram.

Formaldehyde analysis would present the usual problem, but if it were possible to sacrifice one total product mixture (not desirable in this investigation) formaldehyde could be estimated by ordinary chemical methods.

Finally, analysis of such mixtures by gas chromatography would be greatly facilitated if water could be eliminated at the outset. Attempts were made to do this using several common drying agents: calcium chloride, magnesium perchlorate, and anhydrous calcium sulphate. Even the last mentioned removes completely many of the compounds of interest, as well as water, when they are present in small amounts. A simple method for removal of water without effect on small amounts of alcohols, aldehydes and acids would be a valuable contribution to the technique.

Recently several papers describing the analysis of oxidation products have appeared, among them three by C. E. Boord and co-workers: one on products volatile at liquid nitrogen temperature[6], one on analysis of hydrocarbons through the C_7 species[7], and a third on the analysis of oxygen-containing products from the cool flame oxidation of *n*-hexane[8]. Reference to these papers is suggested.

The authors are indebted to the Mass Spectrometry Section of the National Bureau of Standards for mass spectrometric analyses. We have also benefited greatly from many discussions of gas chromatographic techniques with visitors and with colleagues at the Bureau of Standards during the course of this work.

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National Bureau of Standards,
Washington 25, D.C.

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The Detonatability Envelope of Gaseous Fuming Nitric Acid–n-Heptane–Nitrogen Mixtures as a Function of Initial Pressure

R. L. POTTER and D. H. WAYMAN

Detonatability limits for the system fuming nitric acid–n-heptane–nitrogen have been established over initial pressures varying from one half to two atmospheres. At the limits of detonatability, the Chapman–Jouguet temperatures are everywhere above 2 900° K, the majority being about 3 000° K. These limits correlate qualitatively with the rate of decomposition of nitric oxide as the limiting reaction rate in the sequence of reactions in the steady zone.

THE propagation of steady, one-dimensional detonations through an explosive medium has been discussed in detail by J. G. KIRKWOOD and W. W. WOOD[1] including the effects of finite reaction rates. At present, aside from their justification of the Chapman–Jouguet hypothesis, previously obtained in a different way by S. R. BRINKLEY, Jr and J. M. RICHARDSON[2], their analysis of the detailed structure of the detonation wave has been restricted to a discussion of the diameter effect in condensed explosives[3]. To date, little use has been made of the theory because the kinetic data for the numerous reactions occurring in the wave are not available for most systems of practical interest. Since their analysis is for an established steady detonation, even if all the kinetic data were available, it would be a formidable task to try to compute the detonatability envelope of a combustible mixture and hence detonatability envelopes are most easily determined experimentally.

A gaseous combustible medium capable of supporting a detonation may be diluted by a third inert component until it no longer supports a detonation, or either the fuel or oxidizer may be used as diluent for the stoichiometric mixture. The present paper describes experiments which complete the partial results of D. H. WAYMAN and R. L. POTTER[4] on the detonatability envelope of the fuming nitric acid–*n*-heptane–nitrogen gas system at one atmosphere initial pressure. Additional experiments with this same system at one half and two atmospheres initial pressure and at 400° K initial temperature have also been performed. Curves of the theoretically determined detonation parameters are presented for two of these mixtures and some qualitative ideas developed concerning detonation limits are included.

EXPERIMENTAL PROCEDURE

A description of the shock tube apparatus used, the general experimental technique employed, and the electronic equipment used to obtain wave velocity data have been described previously[4, 5]. The *n*-heptane was obtained from Phillips Petroleum Company, Pure Grade; the nitrogen was a commercially available grade purchased from the Air Reduction Company. The fuming nitric acid was purchased from Allied Chemical and Dye Corpn, according to MIL–N–7254B (USAF), Type I (97·5 weight per cent nitric acid minimum). During passage through the shock tube apparatus, the acid was found to decompose, reproducibly. Analysis of condensed samples of hot acid vapours gave the following results, expressed as mole fractions: nitric acid, 0·563; nitrogen dioxide, 0·314; water, 0·044 and oxygen, 0·079; the latter being found by material balance. This decomposed acid composition was used to make the theoretical calculations.

The previous papers[4, 5] describe how the detonatable regions of fuming nitric acid and three hydrocarbon fuels in the gas phase were experimentally determined at one atmosphere initial pressure. Only the modifications in apparatus required to perform the one half and two atmosphere initial pressure experiments with nitric acid–*n*-heptane–nitrogen mixtures are described in detail here.

Figure 1(a) shows schematically the modifications required for the one half atmosphere work. Flows were established and maintained through the reaction tube at one atmosphere pressure and approximately 400°K

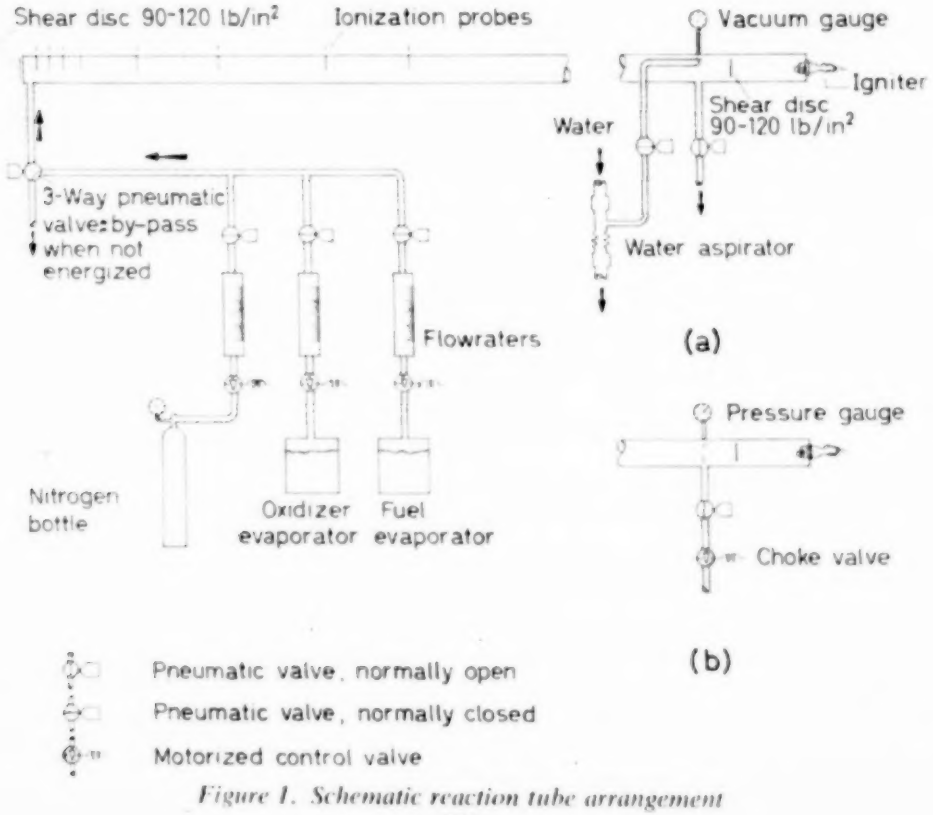

Figure 1. Schematic reaction tube arrangement

until all the air had been swept out. Then the mixtures were trapped in the reaction tube by remotely actuating the pneumatic tube inlet and outlet valves. A water aspirator was used to provide vacuum. A valve to the aspirator was opened to draw off sufficient mixture to produce a total pressure of one half atmosphere of gas mixture in the reaction tube. The pressure was measured with an Ashcroft vacuum gauge, calibrated in inches of mercury, from 0 to 30 in 0·5 in. increments. The total pressure of the gas mixtures was held between 14·5 and 15·5 in. of mercury during this experimental series.

Two shock ignition methods were employed to ignite the combustible gas mixtures. In one, the shock formed by detonating equimolar mixtures of oxygen and acetylene at atmospheric pressure was used. In the other, a shock in the combustible medium was produced by rapidly pressurizing the igniter chamber with helium until a burst disc between the reaction tube and the igniter tube ruptured. Results obtained using the two ignition systems were identical in the one half atmosphere experiments provided that the rupture disc used in the inert gas method was sufficiently strong.

The experiments at two atmospheres initial pressure were performed by inserting a motorized choke valve in the reaction tube outlet line in series with, but downstream from, the outlet valve, as shown schematically in *Figure 1*(b). Flows were established through the reaction tube at two atmospheres pressure and approximately 400°K by suitably adjusting the back pressure with the choke valve. This required separate experimental calibrations of the *n*-heptane and acid flowraters with two atmospheres pressure in the reaction tube. The pressure in the reaction tube was observed with a Crosby pressure gauge, calibrated in pounds per square inch gauge from 0 to 60 in 0·5 in. increments. The total pressure of the gas mixture in the reaction tube was held between 14·5 and 15·5 lb/in^2 gauge (29·2 to 29·7 lb/in^2 abs.) during this experimental series. These mixtures were ignited with the shock arising from the detonation of equimolar oxygen–acetylene mixtures.

As in the previous papers, the data obtained directly from these experiments are a series of time intervals required for the detonation wave to traverse the distance between five small ionization probes set into the wall of the reaction tube at fixed stations. The signals from these probes appear as blanking pulses on a spiral sweep, which is displayed on a DuMont Type 250AH oscilloscope and recorded with a DuMont Type 297 Polaroid Land Camera. The results reported represent an average wave velocity obtained by dividing the total length of the probe intervals by the total elapsed time. Only steady detonations are plotted in the figures; the criteria for a steady wave being that the elapsed time between successive probe stations did not vary by more than the known variance of the thyratron firing times.

An error analysis has been presented previously[4, 5]. Since three flows had to be monitored simultaneously, the error due to these measurements along with the other sources of error, including initial temperature variation, probe spacings, reading the spiral sweep display photographs, crystal time standards, etc., indicate the velocity may be in error by ± 2 per cent. Added

to this there is an error produced by initial pressure deviations from the quoted nominal values so that for the one half atmosphere experiments the velocities can be expected to be accurate to $\pm 2{\cdot}2$ per cent while the two atmosphere results can be expected to be accurate to $\pm 2{\cdot}5$ per cent. As before, only a single reaction tube (3·75 cm i.d.) was used so correction for finite tube diameter was not possible.

The theoretical curves, as before, were computed on an IBM 650 digital computer. It is estimated that the theoretical detonation parameters are good to about 0·25 per cent. Some calculations, mentioned later, not involving the Chapman–Jouguet points, were made by hand. The error in these with respect to temperature may be as high as 2 per cent.

RESULTS

The results of experiments with acid and *n*-heptane gas mixtures at an initial pressure of one half atmosphere are shown in *Figure 2*(a), in which detonation velocity is plotted versus mole fraction of fuel in the mixture. The solid line is the theoretical curve, while the points are experimental values. The results agree favourably with the theoretical velocities. No stable detonations were obtained in mixtures whose compositions were

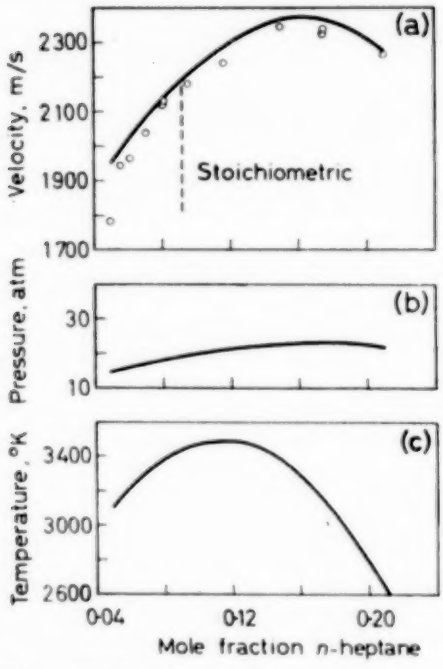

Figure 2. Results obtained using nitric acid–n-heptane gas mixtures with $p_0 = 0{\cdot}5$ *atm,* $T_0 = 400°K$ *and* O_2–C_2H_2 *ignition*

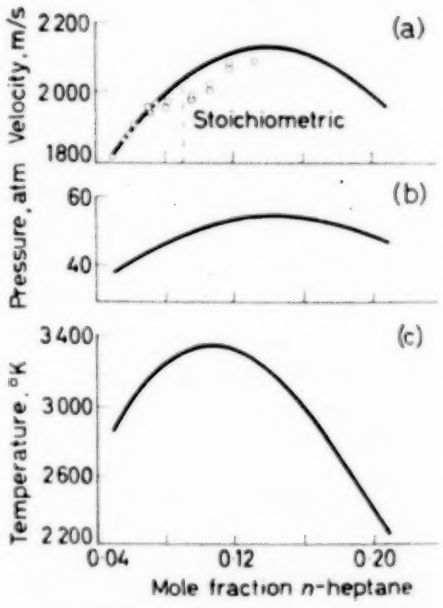

Figure 3. Results obtained using nitric acid–n-heptane–nitrogen gas mixtures, with $p_0 = 2{\cdot}0$ *atm,* $T_0 = 400°K$, O_2–C_2H_2 *ignition and 0·5 mole fraction nitrogen*

further from stoichiometric than the experimental points shown. The theoretical pressures and temperatures for detonations in these mixtures are shown in *Figures 2*(b) and *2*(c), also as a function of the composition.

Results of experiments with nitric acid–*n*-heptane–nitrogen gas mixtures at an initial pressure of two atmospheres and with 50 mole per cent nitrogen

are shown in *Figure 3*(a). In this figure the experimental points are compared with the theoretical curve. Except for a region near stoichiometric, the experimental and theoretical velocities are within the estimated experimental error. Even with 50 mole per cent nitrogen added, the maximum steady state Chapman–Jouguet pressures obtained are greater [*Figure 3*(b)] than those resulting from nitric acid–*n*-heptane detonations at one atmosphere initial pressure. According to our calculations the Chapman–Jouguet pressures resulting from detonations of nitric acid–*n*-heptane are approximately 100 atmospheres when the initial pressure is two atmospheres. Since the present apparatus was not designed to withstand pressures of this magnitude, no tests were made at two atmospheres initial pressure with less than 50 mole per cent nitrogen. When compared to the one atmosphere curve with 50 mole per cent nitrogen dilution (*Figure 7*, $\xi=0{\cdot}5$, ref. 4) the detonation limits are extended further from stoichiometric in both the lean and rich directions. Hence, increasing initial pressure increases the detonatable region with respect to composition.

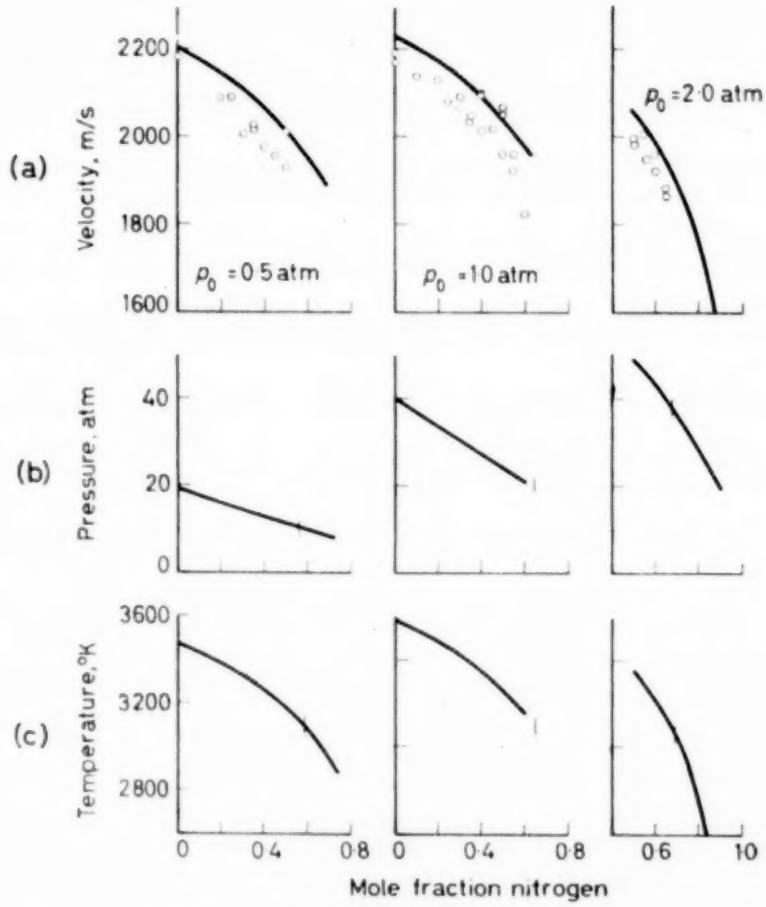

Figure 4. Detonation parameters of nitric acid–n-heptane–nitrogen gas mixtures as a function of nitrogen dilution at three initial pressures with 0·096 mole fraction n-heptane. T_0 = 400° K. O_2–C_2H_2 ignition. The vertical strokes in (b) *and* (c) *represent experimental detonation limits*

The effect of nitrogen dilution on the detonation velocity and the amount of nitrogen required to suppress detonations in nitric acid–*n*-heptane gas mixtures at one half, one and two atmospheres initial pressure are shown in *Figures* 4(a), 5(a) and 6. In *Figures* 4(a) and 5(a), the solid lines are theoretical while the points are experimental data. The agreement between

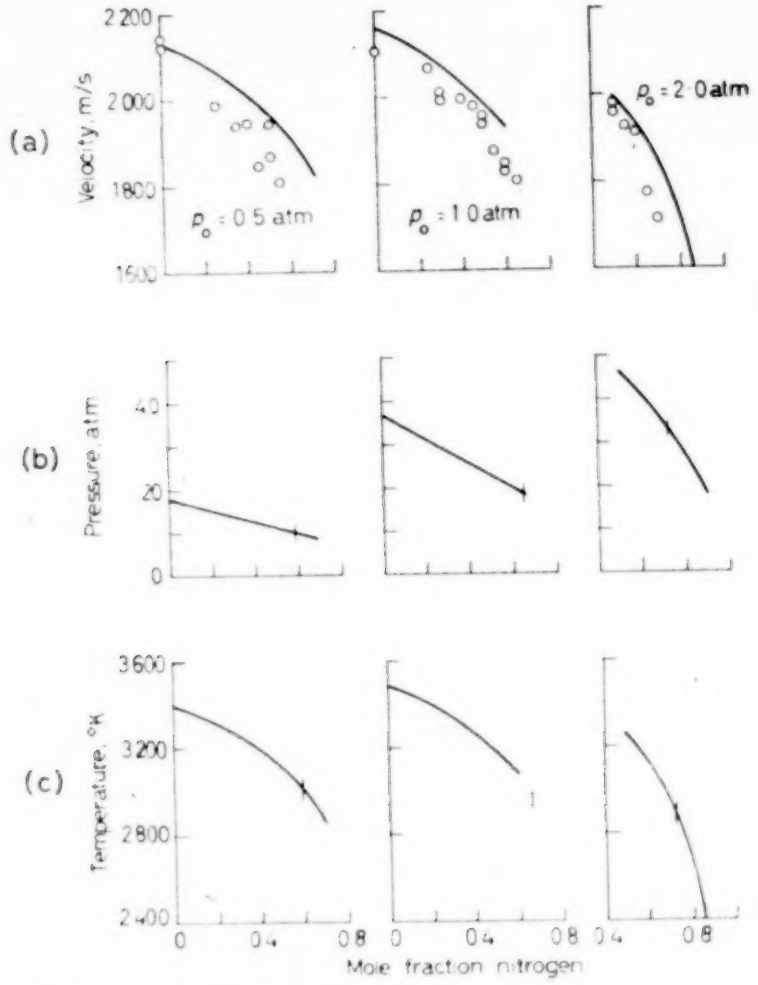

Figure 5. Detonation parameters of nitric acid n*-heptane nitrogen gas mixtures as a function of nitrogen dilution at three initial pressures with 0·081mole fraction* n*-heptane. $T_0 = 400°K$. O_2 C_2H_2 ignition. The vertical strokes in* (b) *and* (c) *represent experimental detonation limits*

experiment and theory is not as good as in the other experimental series but is still considered satisfactory. Only a few points lie outside the limits allowed in the error analysis. The choice of compositions was made to bracket the stoichiometric mixture, which contains 0·091 mole fraction *n*-heptane. From the previous work, these compositions were found to tolerate the greatest nitrogen dilution before detonation was prevented at one atmosphere initial pressure. The data contained in these figures complete the detonatability envelope for the nitric acid–*n*-heptane–nitrogen gas system at one atmosphere.

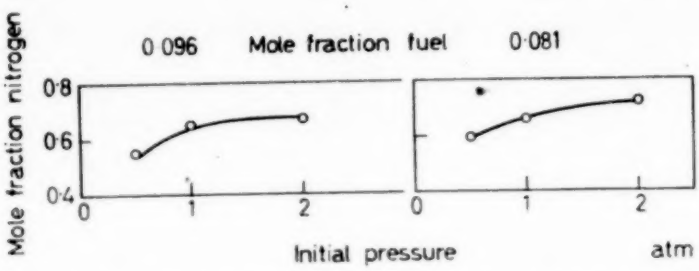

Figure 6. Detonatability limits of nitric acid–n-heptane–nitrogen gas mixtures as a function of initial pressure and nitrogen dilution. $T_0 = 400°K$. O_2–C_2H_2 ignition

The curves shown in *Figure 6* were experimentally determined by plotting the nitrogen dilution at which detonation ceased in nitric acid–*n*-heptane–nitrogen gas mixtures at each of the three initial pressures. From these results it appears that above one atmosphere initial pressure, the concentration of nitrogen required to suppress detonations is quite insensitive to initial pressure.

DISCUSSION OF RESULTS

The experimental results reported here present the detonatability envelope of the system gaseous fuming nitric acid–*n*-heptane–nitrogen as a function of initial pressure. Comparison of the experimental velocities with the theoretical ones shows excellent correlation in the undiluted mixtures at 0·5 atm initial pressure and in the mixtures diluted with 50 mole per cent nitrogen at two atmospheres initial pressure. In general, the experimental velocities fall below the theoretical ones in the dilute mixtures [*Figures 4*(a) and 5(a)]. Part of this may be due to the difficulty of preparing the specified mixture in the tube prior to initiation. Weak mixtures generally show experimental detonation velocities lower than theoretical, and such behaviour has been discussed by G. B. KISTIAKOWSKY *et al.*[6]. Beyond the last points plotted, the mixtures either did not detonate at all or the measured velocity decreased rapidly as the wave progressed down the tube. Since these limits were obtained in a single tube of finite size, they are not identical with the detonatability limits of an infinite plane detonation. However, they are probably a close approximation.

The chemical kinetics involved must determine whether a thermodynamically unstable medium is detonatable. At the limits found in this investigation, the von Neumann shock temperatures (1 550°K) are high enough to ensure that 50 mole per cent of the nitric acid decomposes in less than 0·5 microsecond[7]. This is probably the first reaction in these detonations. Flame studies of nitric acid–hydrocarbon mixtures[8, 9] as well as kinetic studies of the decomposition of nitric oxide[10] strongly suggest that the thermal decomposition of nitric oxide is the slow reaction in these detonations. At the limiting compositions for stable detonations found in this research, the temperature in the steady zone after the von Neumann shock, where the oxidizer has been reduced to nitric oxide, is about 2 400°K. At this temperature, the thermal decomposition of nitric oxide is so slow that it appears unlikely that it can contribute energy to the front.

It is noteworthy that in agreement with other investigators' results for flames[9, 11], detonations in combustible media having species containing oxygen combined with nitrogen as oxidants and hydrocarbons as fuels seem not to be propagated unless the final temperature is of the order of 3 000°K. This is illustrated in *Figures* 4(b), 4(c), 5(b) and 5(c) where the Chapman–Jouguet pressures and temperatures corresponding to the experiments as exhibited in *Figures* 4(a) and 5(a) are shown. The values at the detonatability limits are marked by a vertical stroke. The progression of the pressures at the limits, as the initial pressure is increased while the Chapman–Jouguet temperatures drop slightly, suggests that the rate-determining kinetic process in the sequence of reactions in the steady zone of these detonations is pressure dependent.

According to the idea that the limiting temperature for the existence of stable detonations in the present combustible mixtures is about 3 000°K, it should be possible to form a detonatability envelope for the three component system, nitric acid–*n*-heptane–nitrogen, at any initial pressure by joining the velocities in a velocity versus composition plot at the compositions where the Chapman–Jouguet temperatures are 3 000°K. The information presented in this paper is in agreement with this. The experiments reported previously with nitric acid–methyl *cyclo*pentane and nitric acid–*n*-heptane also conform to this rule[4].

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*The Hydrazine Flame**

M. GILBERT

Experimental data on the hydrazine flame speed are pressure-independent at low pressures. Thus, a second-order reaction mechanism is assumed to be controlling. Kinetics are given for a chain mechanism in which the NH_2 radical is formed by a pseudo-unimolecular process, tending to first order at high pressures, but second order at low pressures. The consequent set of flame equations can be solved using the chemical steady-state hypothesis. In this instance, however, the solution to the flame equation leaves both the flame speed and the overall chemical rate constant undetermined for the hydrazine decomposition. By inserting the experimental flame speed, a value for this rate constant is obtained. It is also possible to calculate the second-order rate constant for the formation of activated N_2H_4 radicals. The rate $k_a \simeq 3 \times 10^{15} \exp(-60\,000/RT)$ cm³/mole sec. The unusually high value for this constant suggests energy transfer to the N-N bond from many vibrational modes of N_2H_4. Re-examination of earlier data of Szwarc on the formation of NH_2 radicals treated as a first-order process indicates that a second-order process may be implied from the data and, also, a value for $k_a \simeq 10^{13} \exp(-60\,000/RT)$ cm³/mole sec may be deduced. Investigation of the validity of the chemical steady state for free radicals in the hydrazine flame is made. It is determined that the flame may only be roughly approximated by the chemical steady state.

RECENT experimental evidence indicates that the laminar gaseous hydrazine (N_2H_4) decomposition flame may belong kinetically to the class of unimolecular reactions which show a transition to a bimolecular rate at low pressures[1-3]. A simple theory for such reactions is given by O. LINDEMANN and C. N. HINSHELWOOD[1]. A detailed chain mechanism for the hydrazine flame is suggested by G. K. ADAMS and G. W. STOCKS[1], but without the characteristics that would yield a rate expression of the Lindemann–Hinshelwood type.

The mechanism of Adams and Stocks leads to a first-order rate which calculates very well the experimental flame speeds at one atmosphere[3-6], using the chemical steady-state hypothesis for intermediate species. Furthermore, the activation energy for the overall mechanism agrees with values derived from flame data. However, difficulty lies in the fact that the experimental flame data show no dependence on pressure below one atmosphere, whereas the first-order flame equation predicts an inverse square-root dependence. For example, at one tenth of an atmosphere, the predicted flame speed would be about three times the atmospheric value, or 600 cm/s, for pure hydrazine decomposition, at an initial temperature of 150°C. The experimental value remains at approximately 200 cm/s down to 30 mm of mercury absolute[2].

In this report, a chain mechanism is presented which does account for all the known experimental evidence. The chain mechanism consists of,

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first, an initiation process of the Hinshelwood type involving production of NH_2 radicals via activation, followed by either collisional deactivation or unimolecular decomposition of N_2H_4. Chain propagation occurs via H, NH_2 and N_2H_3 radicals. Chain termination occurs through various radical recombinations.

Application of the chemical steady-state assumption[5-8] to the hydrazine chain mechanism leads to a rate expression of the Hinshelwood type which becomes second order toward lower pressures, thus accounting for the observed pressure independence of flame speed. P. GRAY and J. C. LEE[3] also recognized the need for a quasi-unimolecular initiation process; however, because of their use of a non-specific model for the mechanism, they were led to choose a final rate expression which differs from that reported here.

One significant aspect of the application of the suggested chain mechanism to the hydrazine flame lies in the value of the specific rate constant obtained for the activation of N_2H_4 molecules. No precise value can be assigned; however, the agreeing values [$\simeq 10^{19} \exp(-60\,000/RT)$], obtained from re-examination of earlier experimental reaction-rate data and, inferentially, from the flame calculation itself must be interpreted by theories of the unimolecular reaction[4, 9, 10].

The symbols used throughout this paper have the following significance:

Nomenclature

B = hot boundary constant (eq. 20)
c = mean specific heat of mixture
D = binary diffusion coefficient
E = activation energy
f = number of vibrational modes excited in N_2H_4
G = fraction of NH_3 in mass rate of flow
G^* = dimensionless fraction of NH_3 in mass rate of flow
[i] = concentration of species i, mole/cm^3
k = chemical rate constants
M = total mass rate of flow per unit area
n = order of reaction
P = total pressure
Q = heat of reaction, cal/g NH_3 formed
R = gas constant, energy units
R_1 = gas constant, mechanical units
t = time
T = temperature
U = gas speed
W_1 = molecular weight of ammonia
X = total concentration of all species P/R_1T, mole/cm^3
α = ratio of Schmidt to Prandtl number
$\beta = (T_m - T_0)/T_m$
γ = time constant, sec^{-1}, for attainment of steady state
ε = mass fraction of NH_3 in mixture
ε^* = dimensionless mass fraction of NH_3
η = dimensionless temperature
λ = mean thermal conductivity
ρ = density of gas mixture
ϕ = fractional deviation from steady-state concentration for NH_2 radical

Subscripts:

m = hot boundary value
0 = cold boundary value

REVIEW OF THE EXPERIMENTAL EVIDENCE

Flame-speed measurements in the almost pure vapour system (97 per cent hydrazine or better) were made in the range 30 to 150 mm of mercury absolute by Hall, using the bunsen flame-area method. These measurements were compared with the measurements made at one atmosphere by R. C. Mc GRAY and A. R. HALL[11]. The measurements were pressure independent, and from the relation $U_0 \propto P^{(n-2)/2}$ (which holds when the flame temperature, as in this instance, is independent or very weakly dependent on pressure) it is found that an overall second-order mechanism ($n=2$) is controlling for flame speed.

Measurements in the vapour system in a constant-volume bomb were made by Gray and Lee in the range 20 to 80 mm of mercury absolute. The burning velocities derived from these experiments were also pressure-independent.

The vapour-phase decomposition rates, obtainable from the linear burning rates of liquid hydrazine strands in small tubes, were studied by Adams and Stocks in the pressure range 1 to 16 atmospheres, and by Gray and Lee in the pressure range 200 to 760 mm of mercury absolute. The linear burning rate essentially measures the mass burning velocity (M) in grammes per unit area per unit time, which, for the gaseous products, is the flame speed multiplied by the density, $\rho_0 U_0$. Thus, the high pressure result of Adams and Stocks that $M \propto P^{1/2}$ corresponds to $U_0 \propto P^{-1/2}$ or $n=1$, and the low pressure result of Gray and Lee that $M \propto P$ corresponds to $U_0 \propto P^0$ or $n=2$. The point of interest here is that, above one atmosphere, a first-order mechanism is indicated; whereas, below one atmosphere, second-order kinetics seem to prevail. These facts are, possibly, the most direct suggestion that hydrazine kinetics are of the Hinshelwood type, since a rate-order transition is exhibited. All the aforementioned flame-speed data, therefore, suggest a quasi-unimolecular mechanism for the hydrazine decomposition flame. Bunsen-flame speed data for pressures above one atmosphere would be of great value in determining the nature of the kinetics.

Additional experimental facts which must be fitted into a flame mechanism are the activation energy, products of combustion, and flame temperature. Both Adams and Stocks, and Gray and Lee find that, from the slopes of Arrhenius plots of flame data as a function of reciprocal temperature, the activation energy for the overall mechanism controlling the flame is of the order of 35 kcal. The data of Adams and Stocks lie in the range 30 to 40 kcal. The more precise data of Gray and Lee give 33 to 36 kcal, the higher value being favoured. Flame mechanisms, with an activation energy of 60 kcal, derived from one-step decompositions as have been suggested in the past, are clearly inadmissible.

Analysis of the combustion products over the entire pressure range in both gaseous and liquid burning systems[1-3, 11] indicates that the homogeneous reaction can be closely approximated by

$$N_2H_{4\,(gas)} \rightarrow NH_3 + \tfrac{1}{2}H_2 + \tfrac{1}{2}N_2 \qquad \Delta H = -33{\cdot}7 \text{ kcal}$$

This result is significant since it marks the hydrazine decomposition as non-equilibrium, the final products failing to correspond to the composition

$N_2 + 2H_2$ at the equilibrium flame temperature, $\sim 1\,400°K$. Flame temperatures measured by Murray and Hall are in reasonable agreement with those calculated for the above reaction ($\sim 1\,950°K$ for an initial temperature of 423°K).

The non-equilibrium character of the flame implies that the reaction mechanism involves, essentially, the freezing out of ammonia as it is formed, i.e. the NH_3 molecule is highly unreactive even at high temperatures. If it is assumed that the NH_3 molecule does not undergo reaction in the chain, then the mechanism must account quantitatively for the NH_3 in the products. By contrast, in an equilibrium situation, NH_3 could form as an intermediate, play an important role in the reaction mechanism, and yet disappear as the system shifts toward equilibrium near the final temperature. Since the latter is apparently not the case, a further restriction is placed on the chain mechanism deduced; namely, that the kinetic scheme produced the final products, NH_3, N_2, and H_2, in the quantitative ratios observed in the reaction given above.

THE FLAME KINETICS AND RATE EQUATION

The following mechanism is suggested as consistent with the experimental facts:

Initiation:		Rate constants
(*1*)	$N_2H_4 + X \rightarrow N_2H_4^* + X$	activation, k_a
(*2*)	$N_2H_4^* + X \rightarrow N_2H_4 + X$	collisional deactivation, k_d
(*3*)	$N_2H_4^* \rightarrow 2NH_2$	unimolecular decomposition, k_r
Propagation:		
(*4*)	$N_2H_4 + NH_2 \rightarrow NH_3 + N_2H_3$	k_4
(*5*)	$N_2H_3 + X \rightarrow N_2 + H_2 + H + X$	k_5
(*6*)	$H + N_2H_4 \rightarrow NH_3 + NH_2$	k_6
Chain breaking:		
(*7*)	$NH_2 + N_2H_3 \rightarrow NH_3 + N_2 + H_2$	k_7
(*8*)	$N_2H_3 + N_2H_3 \rightarrow 2NH_3 + N_2$	k_8
(*9*)	$H + N_2H_3 \rightarrow N_2 + 2H_2$	k_9

For reactions 4 to 9 inclusive, the values of collision diameters and reduced masses indicate that the specific rate constants, k_4 to k_9 inclusive, should agree within an order of magnitude. For present purposes, it will be adequate to assume that they are all equal, their values being taken as $10^{13} \exp(-7\,000/RT)$ as given by E. A. B. BIRSE and H. W. MELVILLE[12] for k_6. Reactions 2 and 3 probably have no activation energy; therefore, an activation energy of 60 kcal is assigned to the activation step, k_a, since this energy is obtained by M. SZWARC[13] as the overall activation energy for the formation of NH_2 radicals. Further questions regarding the nature of the initiation process are discussed below. It may be noted that the decomposition of the N_2H_3 radical is considered bimolecular rather than unimolecular, as assumed by Adams and Stocks. The N_2H_3 radical is not formed in a particularly energetic reaction and, although unstable, it is not likely to contain enough excess energy to make its unimolecular decomposition rate as rapid as decomposition by collision.

If a material balance of the flame mechanism is made, it may be seen from reactions 1 to 9 inclusive that the formation of NH_3, N_2 and H_2 occurs in the ratio 2 : 1 : 1, which is consistent with the analyses of combustion products.

The chemical steady state is now applied to the intermediate species in this mechanism, N_2H_4*, NH_2, N_2H_3 and H, by setting their time derivatives equal to zero and solving for the steady-state concentrations:

$$[N_2H_4^*] = \frac{k_a[N_2H_4][X]}{k_r + k_d[X]} \quad \ldots . [1]$$

$$[H] = \frac{k_5[N_2H_3][X]}{k_6[N_2H_4] + k_9[N_2H_3]} \quad \ldots . [2]$$

Solving for $[N_2H_3]$, the approximation that the steady-state concentrations of [H] and $[NH_2]$ are equal is employed, indication of which was found earlier in the flame mechanism as proposed by Adams and Stocks. With the use of equation 2, and setting k_1, k_5, k_6, k_7, k_8 and k_9 all equal,

$$4[N_2H_3] \simeq -(2[NH_2] + [X]) + \{(2[NH_2] + [X])^2 + 8[NH_2][N_2H_4]\}^{1/2} \quad \ldots . [3]$$

and, since $[X] \gg [NH_2]$, equation 3 reduces to

$$[N_2H_3] \simeq [NH_2][N_2H_4]/[X] \quad \ldots . [4]$$

Now, solving for the steady-state concentration of NH_2 and using the foregoing approximations,

$$\frac{d[NH_2]}{dt} = 0 \simeq \frac{2k_r k_a[N_2H_4][X]}{k_r + k_d[X]} - \frac{k_4 k_7[NH_2]^2[N_2H_4]}{k_5[X]} \quad \ldots . [5]$$

and

$$[NH_2] \simeq \left\{ \frac{2k_r k_a[X]^2}{k_4(k_r + k_d[X])} \right\}^{1/2} \quad \ldots . [6]$$

Referring to the flame mechanism, the following is obtained for the hydrazine decomposition rate

$$-\frac{d[N_2H_4]}{dt} = k_a[N_2H_4][X] - \frac{k_a k_d[N_2H_4][X]^2}{k_r + k_d[X]} + k_4[N_2H_4][NH_2] + k_6[N_2H_4][H] \quad \ldots . [7]$$

From the Hinshelwood theory, the initiation process (represented by the first term in equation 5) is unimolecular at high pressures, when $k_d[X] > k_r$, and bimolecular at pressures low enough that $k_r > k_d[X]$. Regardless of the pressure, the last two terms in equation 7 have been assumed equal. The remaining terms will almost cancel.

Using equation 6, the decomposition rate becomes

$$-\frac{d[N_2H_4]}{dt} \simeq 2k_6[N_2H_4]\left\{ \frac{2k_r k_a[X]^2}{k_4(k_r + k_d[X])} \right\}^{1/2} \quad \ldots . [8]$$

At high pressures, $k_d[X] > k_r$ (note that $k_6 \simeq k_4$), so that

$$\frac{-\mathrm{d}[N_2H_4]}{\mathrm{d}t} \simeq 2{\cdot}8\left(\frac{k_r k_a k_6}{k_d}\right)^{1/2}[N_2H_4][X]^{1/2} \quad \ldots.[9a]$$

At low pressures, $k_d[X] < k_r$ and

$$\frac{-\mathrm{d}[N_2H_4]}{\mathrm{d}t} \simeq 2{\cdot}8\,(k_a k_6)^{1/2}[N_2H_4][X] \quad \ldots.[9b]$$

or, at low pressures, equation 9b may be written as

$$\mathrm{d}[NH_3]/\mathrm{d}t \simeq k\exp(-33\,500/RT)[N_2H_4][X] \quad \ldots.[10a]$$

where the overall rate constant of the reaction is

$$k\exp(-33\,500/RT) = 2{\cdot}8\,(k_a k_6)^{1/2} \quad \ldots.[10b]$$

Equation 10a will account for the pressure independence of flame speed. The activation energy also agrees with experiment. Therefore, the somewhat arbitrary approximations, made in order to obtain equation 10a, may be regarded as tentatively justified. In particular, the approximation that $[H] \simeq [NH_2]$ is recalled.

THE FLAME EQUATION

On the basis of the data of the foregoing section, the steady-state rate expression equation 10a is used for the hydrazine flame. The technique for solving the hydrazine flame equations, including diffusion, has been given[3–7,14].

Defining ε as the instantaneous mass fraction of NH_3 in the reacting mixture at any time, and G as the mass fraction of NH_3 in the flow, the rate of reaction is:

$$\frac{\mathrm{d}[NH_3]}{\mathrm{d}t} = \frac{\rho}{W_1}\frac{\mathrm{d}G}{\mathrm{d}t} = \frac{kP^2\exp(-E/RT)(1-[32/17]\varepsilon)}{R_1^2T^2(1+[32/17]\varepsilon)} \quad \ldots.[11]$$

Equation 11, with the energy balance for the flame and the relation $G = \varepsilon - (\rho D/M)\,\mathrm{d}\varepsilon/\mathrm{d}x$, gives the flame equations:

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}T} = \frac{\lambda(\varepsilon - G)}{\rho D[Q(17/32 - G) - c(T_m - T)]} \quad \ldots.[12]$$

$$\frac{\mathrm{d}G}{\mathrm{d}T} = \frac{\lambda k P^2 W_1 \exp(-E/RT)(1-[32/17]\varepsilon)}{M^2R_1^2T^2[Q(17/32 - G) - c(T_m - T)](1+[32/17]\varepsilon)} \quad \ldots.[13]$$

Introducing the dimensionless variables:

$$\eta = \frac{T_m - T}{T_m - T_a} = \frac{c(T_m - T)}{QG_m}; \quad \beta = \frac{T_m - T_a}{T_m} \quad \ldots.[14]$$

$$G^* = \frac{G_m - G}{G_m - G_a} \quad \ldots.[15]$$

$$\varepsilon^* = \frac{\varepsilon_m - \varepsilon}{\varepsilon_m - \varepsilon_a} \quad \ldots.[16]$$

$$z = \lambda/\rho Dc \quad \ldots.[17]$$

there are obtained, from equations 12 and 13, the dimensionless flame equations for the hot boundary of the flame, where boundary conditions are such that η, G^* and $\varepsilon^* \to 0$; $\varepsilon_m = G_m = 17/32$, and $\varepsilon_0 = G_0 = 0$,

$$d\varepsilon^*/d\eta = z(G^* - \varepsilon^*)/(G^* - \eta) \quad \ldots . [18]$$

and

$$\frac{dG^*}{d\eta} = \frac{B\varepsilon^* \exp[-(E/RT_m)\{\beta\eta/(1-\beta\eta)\}]}{(2-\varepsilon^*)(1-\beta\eta)^2(G^*-\eta)} \quad \ldots . [19a]$$

where

$$B = \lambda W_1 k P^2 \exp(-E/RT_m)/cM^2 R_1^2 T_m^2 \quad \ldots . [19b]$$

The considerations, applied to equations 18 and 19 in order to obtain a solution of the eigenvalue problem for M, are based on the observation that in flame systems in which E/RT_m is of the order of ten or more, the region of the hot boundary largely determines the flame behaviour. In flames governed by the steady-state hypothesis, radical concentrations peak in the region of $\eta \simeq 0{\cdot}1$, as does the reaction rate[7]. Furthermore, in such flames, G^* varies much more rapidly than ε^*, and $G^* \gg \eta$ near the hot boundary. More recondite solutions have been found by T. VON KÁRMÁN[14]. For the approximate treatment of this report, an adequate solution is obtained by applying the foregoing conditions to equations 18 and 19. The first solutions near the hot boundary are:

$$\varepsilon^* = z\eta \quad \ldots . [20]$$

$$G^* = (\tfrac{1}{2}Bz)^{\frac{1}{2}} \quad \ldots . [21]$$

For the second approximation, equation 21 is combined with equation 19a and, after separating variables and considering that $(\frac{1}{2}Bz) \gg 1$, gives:

$$\int_0^1 dG^* = 1 \simeq (2Bz)^{\frac{1}{2}} \int_0^1 \frac{\exp[-(E/RT_m)\{\beta\eta/(1-\beta\eta)\}]}{(2-z\eta)(1-\beta\eta)^2} d\eta \quad \ldots . [22]$$

$$\int_0^1 \frac{\exp[-(E/RT_m)\{\beta\eta/(1-\beta\eta)\}]}{(2-z\eta)(1-\beta\eta)^2} d\eta = \left(\frac{cM^2R_1^2T_m^2}{2\lambda W_1 k P^2 \exp(-E/RT_m)z}\right)^{1/2} \quad \ldots . [23]$$

Using the values $\lambda = 0{\cdot}000\,67$ cal/cm sec °K, $z = 1{\cdot}33$, $Q = 1\,890$ cal/g NH_3, $c = 0{\cdot}66$ cal/g °K, $T_m = 1\,950$°K, $T_0 = 423$°K, $\beta = 0{\cdot}781$, $E = 33\,500$ cal, the RHS of equation 23 is found graphically to have the value 0·082. The following relation is then obtained for the pure hydrazine flame at 1 atm of pressure

$$k/M^2 \simeq 4{\cdot}51 \times 10^{17} \quad \ldots . [24]$$

For an experimental flame speed of 200 cm/s, $M = \rho_0 U_0 = 0{\cdot}184\,5$, and k is $1{\cdot}53 \times 10^{16}$. From equation 10b the value of k_a is then estimated to be $3{\cdot}0 \times 10^{18} \exp(-60\,000/RT)$. It should now be recalled that this value of k_a is a direct result of the inference that the rate equation 9b accounts qualitatively for the known experimental facts concerning the hydrazine decomposition flame and is presumed to yield the proper eigenvalue in the flame-speed equations. A closer look at the activation rate constant k_a

is, therefore, in order, since from a classical point of view, the value of the constant appears so much greater than expected for a second-order activation step.

THE ACTIVATION OF N_2H_4

Before examining the activation process, it is of interest to make reference to the data of M. SZWARC[13] on the rate of formation of NH_2 radicals from hydrazine.

(*a*) *The activation rate, k_a*

This rate, the initiation process in the scheme presented in this report, is given from the steady-state hypothesis as

$$\left\{\frac{d[NH_2]}{dt}\right\}_{\text{initiation}} = \frac{2k_r k_a [N_2H_4][X]}{k_r + k_d[X]} \qquad \ldots [25]$$

Szwarc correlated the experimental data at very low pressures with a first-order rate

$$\left\{\frac{d[NH_2]}{dt}\right\}_{\text{initiation}} = -\frac{2d[N_2H_4]}{dt} = 8 \times 10^{12} \exp(-60\,000/RT)[N_2H_4] \qquad \ldots [26]$$

Equation 26 implies that $k_d[X] \gg k_r$; whereas, the flame behaviour implies the opposite if we accept the Lindemann–Hinshelwood mechanism. However, despite the fact that the activation energy is reasonably well determined by Szwarc's experiments, there may be some doubt as to the validity of a first-order rate for his data. Closer scrutiny indicates that under the laminar heat-transfer conditions prevailing in the reactor tube used by Szwarc, it may not be reasonable to expect radial temperature uniformity for an appreciable distance near the reactor entrance. An approximate analysis was made[15], based largely on the results of L. GRAETZ[16–18], and modified for gas flow[19], showing that the fraction of hydrazine decomposed in Szwarc's non-isothermal reactor, under the major assumptions of velocity and temperature similarity, constant gas properties, and Poiseuille flow, is given by a second-order reaction. If the second-order form of equation 25 is adopted, then

$$-2d[N_2H_4]/dt \simeq 2k_a[N_2H_4][X] \qquad \ldots [25a]$$

Using Szwarc's measured values, $k_a \simeq 10^{19} \exp(-60\,000/RT)$, agreeing with the flame result.

(*b*) *The activation process*

It is recalled that the rate for the flame mechanism was based on the assumption in equations 5 and 8 that at one atmosphere, $k_r \simeq k_d[X]$. Since [X] is of the order of 10^{-5} to 10^{-6} mole/cm^3, it is apparent that $k_r \simeq 10^{-6} k_d$. A further inference which follows if the value of the deactivation rate, k_d, is of the order of the collision number 10^{14} to 10^{15} cm^3 mole^{-1} sec^{-1}, as is reasonable to expect: the value of k_r for the unimolecular decomposition step must be approximately 10^8 to 10^9 sec^{-1}. This value

is in accord with the theories due to O. K. RICE and H. C. RAMSPERGER[20] and to L. S. KASSEL[9], showing that the decomposition reaction 3 has a rate dependent on the specific energy carried by the activated molecule in excess of, roughly, the activation energy.

With regard to the activation rate, k_a, the observed excess over the normal binary collision rate stems from the multiplicity of internal vibrational degrees of freedom for polyatomic molecules. Assuming that activation can occur by energy transfer to a particular bond in question from all degrees of freedom sharing collisional energy, Hinshelwood finds that the normal fraction of molecules, $\exp(-E/RT)$, activated on collision will be increased by the factor

$$(E/RT)^f/(f-1)! \qquad \ldots\ldots[26]$$

where f may be as large as $3n-6$ vibrational modes, or 12 for the N_2H_4 molecule. Values of the order of 10^4 to 10^5 are required to account for observed decomposition rates of nitrogen pentoxide, acetone, azomethane, and other compounds[4, 21]. Other compounds containing the N—N bond also exhibit anomalous behaviour. A calculation made for the N_2H_4 molecule shows that, depending on the temperature chosen, a factor of 10^4 is readily obtained for less than 12 degrees of freedom.

THE PROBLEM OF STEADY STATE

A dynamical-lag criterion for estimating the validity of the chemical steady-state hypothesis for intermediate species was developed in the treatment of the hydrogen bromide flame[7]. The dynamical lag of the flame system is indicated by the ratio of the time required for changes in free radical concentrations to the dynamical time of the flowing gases. The latter is given by the effective flame thickness divided by the mean velocity of the gas through the flame. The characteristic time for free radical concentration change is estimated from the time constant of the reaction. In the hydrazine system, equation 5 gives the rate of change of NH_2 radical as a first approximation

$$d[NH_2]/dt = 2k_a[N_2H_4][X] - k_1[N_2H_4][NH_2]^2/[X] \qquad \ldots\ldots[27]$$

If we consider the flame at steady state at a temperature T_1, and impose an instantaneous temperature jump to T_2, the time for the radical concentration to reach an arbitrary fraction of the steady-state value characteristic of T_2 depends on the time constant of the reaction. Considering equation 27 in terms of this problem, values of k_a, k_1, $[N_2H_4]$ and [X] characteristic of T_2 are assigned, and the equation is integrated with respect to NH_2. The result is given by

$$t = -\frac{1}{\gamma}\ln\phi + \frac{1}{\gamma}\ln\left(\frac{[NH_2]_{T_2} + [NH_2]}{[NH_2]_{T_2} + [NH_2]_{T_1}}\right) \qquad \ldots\ldots[28]$$

where

$$\gamma = 2([N_2H_4]\{2k_ak_1\}^{1/2})_{T_2} \qquad \ldots\ldots[29]$$

$$\phi = \frac{[NH_2]_{T_2} - [NH_2]}{[NH_2]_{T_2} - [NH_2]_{T_1}}; \quad \phi_{(t=0)} = 1, \quad \phi_{(t=\infty)} = 0 \qquad \ldots\ldots[30]$$

and the T_2 and T_1 subscripts refer to steady-state values of $[NH_2]$ given by $\{2k_a[X]^2/k_1\}^{1/2}$. For small temperature intervals, equation 28 reduces to

$$\phi \simeq \exp(-\gamma t) \qquad \ldots [3]$$

where $1/\gamma$ is the time constant for ϕ to fall to $1/e$, ϕ being the fractional deviation from steady state.

For the hydrazine flame, the minimum value for the time constant, particularly in the high-temperature region of the flame, is $\sim 10^{-6}$ sec. For an experimental flame speed of 200 cm/s at 1 atm, the estimated flame thickness is 0·007 cm, and the estimated overall dynamical time is 10^{-5} sec. It is, therefore, apparent that the steady-state approximation is of borderline validity, since the ratio of chemical time to dynamical time is in the range 0·1 to 1·0.

In regions of the flame where the time constant may be larger (up to 10^{-5} sec) the steady state must fail. It is evident that this is the situation from calculations of G. MILLÁN and S. SANZ[6] and of D. B. SPALDING[22] which show that the actual radical concentrations are of the order of steady-state values in the active region of combustion, but exceed steady state considerably below this temperature and fail to attain steady-state values very close to the hot boundary. The excursions of the actual radical concentrations, however, are much less than an order of magnitude, which accounts for other investigations showing negligible effect on flame-speed calculations. Consequently, the hydrazine flame, particularly in view of the relatively large radical concentrations (mole fractions up to 0·1), must be considered as only roughly approximated by a steady-state model.

CONCLUSIONS

An attempt has been made to elucidate the mechanism of the hydrazine decomposition flame by finding a chain reaction which is consistent with experimental flame data. The decomposition is suggested to be of the Hinshelwood type, unimolecular at high pressures, bimolecular at low pressures, with the transition occurring around one atmosphere. The latter fact probably explains why a classically unimolecular rate was successful earlier in calculating flame speeds at one atmosphere, although the pressure dependence was incorrectly indicated.

The activation process is indicated to be complex and to involve contributions to energy square terms from many vibrational modes of the hydrazine molecule, thus yielding a large activation rate constant of the order of 10^5 to 10^7 times the normal bimolecular frequency factor. The decomposition reaction of the activated hydrazine molecule is indicated to have a rate constant many orders of magnitude lower than the unimolecular frequency factor. This fact is consistent with the predictions of Rice and Ramsperger and of Kassel regarding unimolecular decompositions of activated species.

An examination of the time constant for free-radical reaction, compared with the probable dynamical time for the fast decomposition flame, indicates that the chemical steady state is not realizable in the chain mechanism, and sizable deviations can be expected. Fortuitously, in the doubtful cases

the excursions of the radical concentrations fall above and below the steady-state values, providing partial cancellation of the deviations. Thus, the general success of flame-speed calculations, using both steady-state and non-steady-state methods, is not surprising.

The maximum free-radical concentrations implied by the treatment given in this report are of sizable order of magnitude (mole fractions $\sim 0{\cdot}1$). It is expected, therefore, that large concentration gradients will be found within the flame, as a first approximation. Particularly in the case of hydrogen atoms, diffusion would then suppress the steady-state profile to a considerable degree, making it similar in shape to the non-steady-state profiles calculated by Millán.

Hydrazine diluted with water gives decomposition flames that appear to obey kinetics similar to the pure decomposition flame. Thus the role of water vapour in the decomposition kinetics at low temperatures appears only to be that of a third body and an inert diluent. On the other hand, the kinetics of hydrazine–oxygen flames are probably more complex than those of the decomposition flame, which, considering the complexity of the mechanism already presented in this report, points to a formidable kinetics problem.

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*Kinetics of Hydrazine Decomposition in a Laminar Non-isothermal Flow**

M. GILBERT

The experimental results on the decomposition of hydrazine are re-examined. The assumption is made that a dilute hydrazine-toluene gas mixture at low pressure will not undergo isothermal reaction under the flow conditions experienced in the apparatus used by Szwarc, but that there will be a strong effect due to heat transfer in the entrance region of the reactor. Analysis of the non-isothermal reactor leads to reinterpretation of the experimental rate data. The existing data are found to favour a second-order formation for NH_2 radicals, rather than a first-order formation. The rate constant is approximately $10^{13.9}\exp(-60\,000/RT)$ cm³/mole sec, which appears to be the low-pressure value in a quasi-unimolecular rate process.

THE application of laminar-flame theory to the gaseous hydrazine flame involves the use of a chain mechanism[1]. This chain mechanism must be of the second-order overall, to account for the experimental facts concerning flame speed, activation energy, and pressure dependence below one atmosphere.

The chain mechanism which fulfils the necessary requirements is found to have a quasi-unimolecular initiation process: that is, the propagating NH_2 radicals are formed in a Hinshelwood–Lindemann mechanism (second-order at low pressures). The flame theory, with the use of this mechanism, permits an estimate of the rate of activation of hydrazine, which is bimolecular.

The motivation for the present paper lies in the fact that the experimental data of Szwarc on hydrazine decomposition in a heated tubular reactor[2] were interpreted to indicate a simple first-order formation of NH_2 radicals at low pressures, rather than a second-order formation such as that which seems to be required by flame theory. A closer inspection of Szwarc's data was worthwhile, to determine whether a second-order formation rate for NH_2 could be established from the data.

The basis of Szwarc's analysis is as follows. If the hydrazine decomposition is assumed to take place in an isothermal reactor, then the rate data favour the first-order NH_2 formation. However, a slight dependence of the specific rate constant on the absolute pressure was noted (tending to support second-order NH_2 formation), but was dismissed as not significant. The present analysis, using the same experimental data, assumes that the conditions in the tubular reactor are probably isothermal only in the downstream portion and are non-isothermal near the entrance. The results definitely indicate a second-order NH_2 formation; thus, the experimental kinetic data of Szwarc become consistent with the results of flame data.

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The interpretation of kinetic data obtained in flow through a heated reactor is thus found to be sensitive to the boundary conditions imposed by the experimental apparatus (the inlet flow and temperature, the heating oven, etc.). Physical conditions in flow reactors must therefore be established with considerable care. At the least, there is need to know well the actual boundary conditions.

The symbols used throughout this paper have the following significance:

Nomenclature

a = reactor radius
c = constant (eq. 8)
d = reactor diameter
E = activation energy
Ei = exponential integral
G = mass flow of mixture, g/s
[i] = concentration of species
k = specific chemical rate constant
L = reactor length
$\bar{m}$ = average molecular weight
M = total species
P = total pressure
P_r = Prandtl number
Q_0 = volume flow through reactor at entrance conditions
R = gas constant, 1·987 cal/mole °K
R_1 = gas constant, 82·06 cm³ atm/g mole °K
R_e = Reynolds number
T = temperature
$T(x, y)$ = gas temperature in reactor at position x along the axis and at radius y
t_c = contact time
U = gas velocity
$\bar{U}$ = average gas velocity
$U_{m,0}$ = maximum gas velocity at entrance
V = reactor volume
x = distance from reactor entrance
z = mole fraction of hydrazine
$\bar{z}$ = average mole fraction of hydrazine in reactor
κ = thermal diffusivity
μ = fluid viscosity
ψ = fraction of hydrazine disappearing
ρ_a = mixture density at wall conditions

Subscripts:

a = wall conditions
0 = entrance conditions
1 = first-order kinetics
2 = second-order kinetics

THE ISOTHERMAL REACTOR

Before consideration of the non-isothermal reactor with chemical reaction in a flow, Szwarc's treatment of the constant-pressure isothermal case is briefly reviewed. The temperature of the entering fluid is assumed to rise instantaneously to the reactor wall temperature T_a. Thus, if the total mass flow and the fraction of reactant (hydrazine) in the flow are known, then the fraction decomposed in the reactor is:

$$\psi = \frac{S(a)V}{Q_0[N_2H_4]_0} = \frac{S(a)\rho_a V}{G[N_2H_4]_0} = \frac{S(a)R_1T_a t_c}{z_0 P} \qquad \ldots [\ ]$$

where $S(a)$ is the decomposition rate, and t_c is the contact time $(L/\bar{U})$ in the reactor. Thus, $S(a)$ is given by a first-order rate

$$S_1(a) = k_1 \exp(-E/RT_a)\,[N_2H_4]\ \text{mole/cm}^3\ \text{sec} \qquad \ldots.[2]$$

The second-order rate is given by

$$S_2(a) = k_2 \exp(-E/RT_a)\,[N_2H_4]\,[M]\ \text{mole/cm}^3\ \text{sec} \qquad \ldots.[3]$$

Introduction of equations 2 and 3 in equation 1 results in fractions decomposed:

$$\psi_1 \simeq \bar{z} k_1 \exp(-E/RT_a)\, t_c / z_0 \qquad \ldots.[4]$$

$$\psi_2 \simeq \bar{z} k_2 \exp(-E/RT_a)\, Pt_c / z_0 R_1 T_a \qquad \ldots.[5]$$

It may be seen that the isothermal constant-pressure reactor shows a linear pressure dependence of ψ for the second-order decomposition and no pressure dependence for the first-order rate. Pertinent data from Szwarc are given in columns 1 and 2 of *Table 1*. For three pairs of similar runs, the pressures are roughly in the ratios of 1 : 1·5 : 2·5, whereas the corresponding fractions decomposed are experimentally in the ratios 1 : 1·2 : 1·6. Thus, the measured fractions decomposed are neither independent of nor linearly dependent on pressure but, from the few data presented, appear to depend on the square root of pressure. A clear choice of mechanism is not obvious.

Table 1. Tests of alternative equations for fraction of hydrazine decomposed

Test	*Total pressure* atm*	*Fraction decomposed* (measured)*	$R_{c,a}$	*Fraction decomposed*	
				Eq. 9	*Eq. 10*
				Normalized at	*Normalized at*
53	0·00660	0·170	18·8	0·170	0·170
52	0·00663	0·192	18·9	0·186	0·187
31	0·00990	0·204	31·4	0·145	0·219
32	0·00969	0·226	31·0	0·133	0·196
48	0·01547	0·288	45·6	0·122	0·284
46	0·01650	0·298	47·8	0·103	0·253

*Data from M. Szwarc[3].

THE NON-ISOTHERMAL REACTOR

One is led to believe that the significant fact is the failure of the data to be clearly independent of pressure; the apparent square-root dependence on pressure of the decomposition is probably incidental and less essential. The obvious course, in view of the probable reliability of Szwarc's measurements, is to look for an answer in the poorly defined flow and thermal conditions of the reactor. Therefore, one proceeds to analyse the problem of a laminar flow with heat transfer, and with a gas-phase reaction of very low intensity occurring simultaneously in a non-uniform temperature field. The latter is established by the heat transfer from the tube walls.

At the outset, the experimental results may be anticipated in the following qualitative argument. The experimental non-isothermal reactor is considered to be composed of an entrance region or volume of no reaction, followed by a practically isothermal reacting region. This assumption is reasonable, because the large value of the exponent in equations 2 or 3 ($E/RT \gg 1$)

causes the rate to fall very rapidly for values of T only slightly less than T_a. For this model, the fraction decomposed can be immediately written in a form similar to equation 1, as

$$\psi \simeq S(a)(V - V_e)/Q_0[N_2H_4]_0 \quad \ldots [6]$$

where V_e is the entrance volume of no reaction. The reacting volume is $V - V_e$. Obviously, for the cylindrical reactor, V_e is proportional to the axial distance x_e required for the gas temperature to attain a value close to T_a.

The entrance volume, or axial distance, can be estimated from the law subsequently assumed for the growth of axial temperature:

$$\frac{T_a - T(x,0)}{T_a - T_0} \simeq \exp(-14{\cdot}63\,\kappa x/U_{m,a}d^2) = \exp(-14{\cdot}63\,x/R_eP_ad) \quad \ldots [7]$$

Moreover, when the LHS of equation 7 is equal to a fixed (small) number based on $T(x,0)$ approaching a value near T_a, it is clear that x_e is proportional to the Reynolds number. Therefore, x_e and V_e are directly dependent on the pressure. As a result, equation 6 can be cast in the form

$$\psi \simeq \frac{S(a)V(1 - cP)}{Q_0[N_2H_4]_0} \quad \ldots [8]$$

Equations 1 to 3 show that the coefficient of the quantity $1 - cP$ is independent of P and linear with P for first- and second-order reactions, respectively. The quantity $1 - cP$ itself obviously varies inversely with pressure and, over limited regions, can be approximated by P^{-n}, where n lies between 0 and 1, depending on the entrance conditions. Thus, qualitatively, in the non-isothermal reactor one should find ψ to depend on the pressure as P^0 to P^{-1} for a first-order reaction and as P^0 to P^1 for a second-order reaction. As pointed out in the discussion of the isothermal reactor, the experimental data show a $P^{1.2}$ dependence; thus, the qualitative model indicates a second-order mechanism.

A detailed mathematical description of the non-isothermal reactor is given elsewhere by the present author[2] and is summarized in the Appendix. An expression is developed for the decomposition rate which more closely represents the experimental reactor; finally, with the available experimental data, a cogent distinction is permitted by the detailed model between the two forms of reaction rate.

The physical model which fits the existing hydrazine-decomposition experiments can be described as follows. Consider laminar flow in a tubular reactor. At a point along the length, a discontinuous change in wall temperature occurs. Heating and reaction in the fluid ensue. The fluid density is so low that natural convection can be neglected (Grashof numbers < 1000). The mole fraction of the reactant (N_2H_4) in the fluid (mostly toluene) is very small, so that the thermal effects of the reaction are also negligible. The fluid velocity is sufficiently great that the amount of reaction per unit length of tube is very small. Thus, axial gradients in concentration and pressure can be neglected. Axial and radial diffusion are negligible. Because the total change in the mole fraction of N_2H_4 in

the tube is small, a constant average value is used as a first approximation.

It is assumed that the radial velocity and temperature distributions are similar and obey the Poiseuille law. Although the velocity distribution can be so regarded without great error, especially if a sufficiently long approach section exists, the temperature distribution at the entrance of the heating section must deviate greatly. The fluid viscosity is assumed constant.

It is well known, however, from the solution of the heat-transfer problem for incompressible Poiseuille flow, that the similarity condition is good beyond several tube diameters downstream of the entrance[4-6]. Furthermore, consideration of the compressible-flow case with large temperature and viscosity increases in the gas[7], such as those which occur in the present case, shows that the temperature and velocity profiles deviate from the Poiseuille law, even in downstream conditions. The profiles become more peaked toward the axis as the flow proceeds downstream. However, a sort of similarity (not parabolic) appears to be preserved.

With the assumptions noted above, the description of the non-isothermal reactor may be further examined. The peaked profiles tend to cause relatively more mass to flow through the central region of the tube than does Poiseuille flow. Thus, in the treatment of the reactor, the Poiseuille-flow assumption will exaggerate the influence of the high-temperature fluid near the wall. In this regard, the Poiseuille assumption will under-estimate the deviation from an isothermal-reactor situation. The similarity assumption, though it be invalid, enables one to obtain a simple solution for comparison purposes; however, it will also under-estimate the radial temperature variation, particularly near the reactor entrance. Here, again, the wall-temperature influence is unduly emphasized. Clearly, the difference between the isothermal reactor and the non-isothermal reactor will be under-estimated by the aforesaid assumptions.

Only the assumption of constant fluid viscosity tends to over-estimate non-isothermal effects. In the analysis, however, the fluid viscosity is taken at the entrance conditions of the fluid, where the reactor behaviour is mainly determined. Thus, the failure to account for a threefold change in viscosity leads to no serious error.

In obtaining the non-isothermal-reactor behaviour, an expression is first given for the rate of disappearance of hydrazine per unit volume at a point in the fluid stream. Taking into account the radial temperature variation, an average value of the rate of disappearance in the cross sectional area is calculated. Then, taking account of the axial change of fluid temperature, the rate of disappearance is averaged over the entire reactor volume. The total amount of reactant decomposed is readily calculated and compared with experimental data.

RESULTS OF ANALYSIS

The fraction of hydrazine decomposed in the reactor for a first-order chemical-reaction rate is given by

$$\psi_1 \simeq \frac{Pk_1 [\exp(-E/RT_a)] (P_r)\, d^2 \overline{m}\, z_a g(Z')}{14{\cdot}63\, \mu_a z_a R_1 T_a} \qquad \ldots [9]$$

and, for a second-order rate, by

$$\psi_2 \simeq \frac{P^2 k_2 [\exp(-E/RT_a)](P_r)\, d\, \bar{m}\, z\, g(Z')}{14{\cdot}63\, \mu_0 z_0 R_1^2 T_a^2} \quad \ldots [11]$$

where

$$g(Z') = (1/Z')[1 - \exp(-Z')] - \mathrm{Ei}(-Z') \quad \ldots [11]$$

and

$$Z' = \frac{E(T_a - T_0)}{RT_a^2} \exp\left(-\frac{14{\cdot}63}{R_1 P_r}\frac{L}{d}\right) \quad \ldots [12]$$

It is possible to review the data of Szwarc[2] on the hydrazine fraction decomposed, using those relations derived for a non-isothermal reactor. A comparison of equations 9 and 10 with equations 4 and 5 shows that, if the reaction is taking place under non-isothermal conditions, the pressure dependence of ψ is complex for both first- and second-order-reaction kinetics. This is essentially the effect of the Reynolds number. As the Reynolds number approaches zero (under conditions of extremely low velocity), the reactor naturally approaches the isothermal case, and the pressure dependence will again be as given by equations 4 and 5.

A test of the experimental data, using the non-isothermal relations, is shown in *Table 1*, where the pressure and fraction decomposed are obtained from Szwarc's data. The entrance Reynolds numbers are based on data supplied by Szwarc[5] on the measured mass flows of toluene and on the reactor diameter (approximately 2·3 cm). At an entrance temperature of 300° K, the fluid viscosity is estimated as 7×10^{-5} g/cm sec. The Reynolds numbers are shown in column 4 of *Table 1*. Columns 5 and 6 are calculations based on equations 9 and 10, normalized to give the value for the fraction decomposed in test 53. Thus, the succeeding values are comparisons of the relative efficacies of equations 9 and 10 in predicting the trend of the data.

Equation 10, based on the second-order decomposition rate, predicts the trend of the data in a rather striking manner, but equation 9 fails to do so. Thus, in contrast to the inconclusive showing of first-order kinetics in an isothermal reactor, the present non-isothermal treatment clearly points to a second-order reaction. It must be mentioned that all the applicable experimental data of Szwarc was analysed. The results were the same as for the data presented here with the trends appearing similar to *Table 1*, with better or worse agreement depending on the scatter of the original data. *Table 1* is merely representative.

CONCLUSION

The analysis indicates that the kinetics of hydrazine decomposition should obey equation 3. As is shown by the present author in a previous paper[1], these kinetics are in agreement with those deduced from flame studies. The decomposition of hydrazine would thus appear to follow a quasi-unimolecular process for the formation of NH_2 radicals.

Assuming that a second-order law holds for Szwarc's data, one may calculate the rate constant k_2 to be approximately $10^{19} \exp(-60\,000/RT)$

cm^3/mole sec, rather than $4 \times 10^{12} \exp(-60\,000/RT)\ sec^{-1}$, as deduced for first-order kinetics. The implications of the former value in regard to activation of N_2H_4 molecules are also discussed in the previous paper[1].

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APPENDIX

DESCRIPTION OF THE NON-ISOTHERMAL REACTOR

The average reaction rate

The molar rate of disappearance of hydrazine per unit volume of mixture, at an axial distance x from the start of heating and a radial distance y from the tube axis is given by $S(x, y)$ mole/cm^3 sec. The velocity at this point is $U(x, y)$. The wall temperature T_a is assumed constant in the heating section. The average rate of reaction over the cross section is

$$\bar{S}(x) = \frac{2}{a^2}\int_0^a S(x, y)\, y\, dy \qquad \ldots [13]$$

and the average rate of reaction over the entire reactor is

$$\langle S \rangle = \frac{1}{L}\int_0^L \bar{S}(x)\, dx \qquad \ldots [14]$$

The first- and second-order forms of $S(x, y)$ are given by

$$S_1(x, y) = k_1 [N_2H_4(x, y)] \exp[-E/RT(x, y)] \qquad \ldots [15]$$

$$S_2(x, y) = k_2 [N_2H_4(x, y)] [M(x, y)] \exp[-E/RT(x, y)] \qquad \ldots [16]$$

The assumptions of Poiseuille flow and velocity and temperature similarity give $\eta = (y/a)^2$. One defines

$$\eta(x, y) = \frac{T(x, y) - T(x, 0)}{T_a - T(x, 0)} \qquad \ldots [17]$$

$$\beta(x) = \frac{T_a - T(x, 0)}{T(x, 0)} \qquad \ldots [18]$$

so that

$$T(x, y) = T(x, 0)[1 + \beta(x)\,\eta(x, y)] \qquad \ldots [19]$$

The above relations lead to an integral for $\bar{S}_2(x)$,

$$\bar{S}_2(x) = S_2(a)\,\frac{T_a^2 \exp[-E/RT(x, 0)]}{T^2(x, 0)\exp[-E/RT_a]} \int_0^1 \frac{\exp\left[\dfrac{E}{RT(x, 0)}\,\dfrac{\beta(x)\,\eta(x, y)}{1 + \beta(x)\,\eta(x, y)}\right]}{[1 + \beta(x)\,\eta(x, y)]^2}\, d\eta \qquad \ldots [20]$$

where $S_2(a) = S_2(x, a)$ is given by $\bar{z} k_2 P^2 \exp(-E/RT_a)/(R_1 T_a)^2$. A similar relation holds for $\bar{S}_1(x)$. By use of exponential integrals, noting that $E/RT \gg 1$, one obtains the results:

$$\bar{S}_1(x) \simeq \frac{S_1(a)}{\beta(x)} \frac{RT_a}{E} \frac{T_a}{T(x,0)} \left[1 - \frac{T(x,0)}{T_a} \exp\left\{ - \frac{\beta(x) E}{RT_a} \right\} \right] \quad \ldots [21]$$

$$\bar{S}_2(x) = \frac{S_2(a)}{\beta(x)} \frac{RT_a}{E} \frac{T_a}{T(x,0)} \left[1 - \exp\left\{ - \frac{\beta(x) E}{RT_a} \right\} \right] \quad \ldots [22]$$

The values of $\langle S \rangle$ are found by using the law for axial temperature growth given earlier (equation 7) which provides a relation for $T(x,0)$. There is eventually obtained from the foregoing equations, with the exponential integral,

$$\langle S \rangle_1 \simeq S_1(a) \frac{d}{L} \frac{R_c P_r}{14{\cdot}63} \left[\frac{RT_a^2}{E(T_a - T_0)} \exp\left\{ \frac{14{\cdot}63}{R_c P_r} \frac{L}{d} \right\} \left(1 - \exp\left\{ - \frac{B\phi_L}{T_a} \right\} \right) - \frac{RT_a^2}{E(T_a - T_0)} - \mathrm{Ei}\left(- \frac{B\phi_L}{T_a} \right) \right] \quad \ldots [23]$$

$$\langle S \rangle_2 \simeq S_2(a) \frac{d}{L} \frac{R_c P_r}{14{\cdot}63} \left[\frac{RT_a^2}{E(T_a - T_0)} \exp\left\{ \frac{14{\cdot}63}{R_c P_r} \frac{L}{d} \right\} \left(1 - \exp\left\{ - \frac{B\phi_L}{T_a} \right\} \right) - \mathrm{Ei}\left(- \frac{B\phi_L}{T_a} \right) \right] \quad \ldots [24]$$

where $\phi_L = \exp(-14{\cdot}63\, L/R_c P_r d)$ and $B = E(T_a - T_0)/RT_a$.

For conditions encountered in an actual case $T_a = 300^\circ$K, $T_a = 1\,000^\circ$K, $E = 60\,000$ cal/mole, $L/d = 10$, $R_c \simeq 55$, $P_r \simeq 0{\cdot}63$. Thus one finds that $\langle S \rangle_1$ and $\langle S \rangle_2$ are about $0{\cdot}4\, S_1(a)$ and $0{\cdot}4\, S_2(a)$ respectively. In such a non-isothermal reactor the overall reaction takes place at 40 per cent of the reaction rate near the wall.

Total decomposition in the non-isothermal reactor

Since the amount of decomposition occurring per second is $\pi d^2 L \langle S \rangle / 4$ one can find the fraction ψ of input hydrazine ($\pi d^2 U_a z_a P / 4 R_1 T_a$) decomposed in the reactor

$$\psi = \frac{\langle S \rangle L R T_a}{z_a \bar{U}_a P} \quad \ldots [25]$$

which leads, from equations 23 and 24, to the first- and second-order expressions given earlier as equations 9 and 10.

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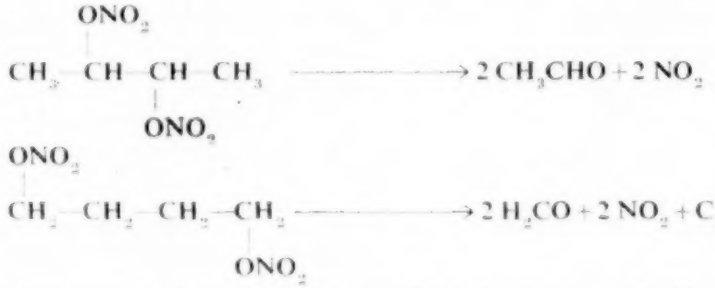
The Combustion of the Butane-2,3- and 1,4-Diol Dinitrates and Some Aldehyde–Nitrogen Dioxide Mixtures

J. POWLING and W. A. W. SMITH

Decomposition flames of butane-2,3-diol dinitrate and butane-1,4-diol dinitrate have been studied at atmospheric pressure by stabilizing flat flames upon the liquid surfaces and measuring product concentrations and temperature profiles. Products were generally analysed by infra-red methods, and an in situ *spectroscopic method in the visible region has been employed to estimate the significant nitrogen dioxide concentrations in the flames. The results indicate that these esters, in contrast to those mononitrates so far studied, break down in a unimolecular fashion, overall reactions being:*



Brief examinations of the flames of acetaldehyde–nitrogen dioxide mixtures and formaldehyde–nitrogen dioxide–ethylene mixtures have been made for comparison with those of the nitric esters, to which, in fact, they show a great similarity.

THE decomposition flames (in the absence of air) of liquid ethyl nitrate, *n*-propyl nitrate and *iso*propyl nitrate have already been studied[1, 2] in the laboratory at atmospheric pressure using the flat flame technique. On the evidence of detailed analyses of the earliest reaction products in these flames it was suggested that degradation of the nitric ester was brought about mainly by nitrogen dioxide and nitrous acid attack in a short chain mechanism. Such a process could account in a simple way for all the diverse reaction products of these esters. The products from the flame decomposition at atmospheric pressure are not, of course, in thermodynamic equilibrium.

There is reason to believe, however, that certain dinitrates and trinitrates do not burn in the same way as the above mentioned mononitrates. G. K. ADAMS and L. J. DRUMMOND[3] in an investigation of the rates of burning of a variety of nitric esters found that, at constant heat of explosion, the rates were dependent upon the chemical structure. An example of this was that the 1,4- and 2,3-butanediol dinitrates, in spite of slightly higher heats of explosion than ethyl nitrate, burned at only half the rate of the latter.

It was considered worth while, in the present studies of the effect of chemical structure on the mechanism of degradation of nitric esters, to consider the combustion of butane-2,3-diol dinitrate (2,3-BDDN) and butane-1,4-diol dinitrate (1,4-BDDN) to see if any fundamental difference between their mechanism of combustion and that of the mononitrates could be observed.

In the course of the work on both dinitrates it became apparent that the reactions of nitrogen dioxide with aldehydes or olefines were vital parts of the overall combustions and a brief study of the flames of certain mixtures of these materials was undertaken. Nitrogen dioxide–acetaldehyde vapour flames were examined in a flow system using a flat flame burner and nitrogen dioxide–formaldehyde–ethylene flames in a heated static system.

EXPERIMENTAL METHOD

Flame stabilization

Flat, stationary decomposition flames of the nitrates were stabilized at atmospheric pressure in an inert gas in a burner similar to that already described in the ethyl nitrate work[1] with the exception that a smaller burning surface had to be employed ($\sim 3\ cm^2$) because of the limited supply of the esters. Temperature and reaction product profiles were obtained by covered thermocouple measurements and extraction of samples from the flame.

The premixed acetaldehyde–nitrogen dioxide flames were studied using a flat flame gas phase burner of 2·3 cm i.d. The flames were invisible in ordinary laboratory light and were located by means of shadow technique. The temperature gradients in the flames were not steep enough to give very well-defined shadows but the combination of the latter with the disappearance of the brown nitrogen dioxide colour enabled the flame front to be accurately located. The fuel lines, flow meters, etc., were heated electrically to prevent condensation. The nitrogen dioxide was used as supplied (Rubber Industries and Sherman Chemicals Ltd) and its purity was expected to be 98 per cent. Care had to be taken concerning supplies of acetaldehyde, some of which were found to contain large quantities of paraldehyde.

Steady flow of reactants was obtained by immersing the storage cylinders, including the controlling valves, completely in thermostatic baths ($\sim 60°C$ for acetaldehyde, $\sim 40°C$ for nitrogen dioxide) so that adequate reserves of gas pressure were available.

Flames of nitrogen dioxide–formaldehyde–ethylene which were required for comparison with that of 1,4-BDDN were not stabilized as stationary flames because of the difficulties envisaged of supplying copious quantities of gaseous formaldehyde. Instead, mixtures were made up in a vertical heated flame tube 5 cm in i.d. and 25 cm long, and ignited at the lower end. The flames propagated upwards through the mixture and the pressure in excess of one atmosphere (absolute) was released from the bottom by a large valve. The final products of reaction were removed from the tube (by a Toepler pump via a cold trap) for analysis.

Product analysis

Variations of the analytical techniques were, of course, necessary in the different systems, but basically the methods were the same as those previously described[1, 2] and will not be considered in detail here except where significant changes were made. The extracted samples were divided into three main fractions by passing them directly from the probe into a trap maintained at approximately −140°C. This gave a gaseous fraction and condensate, the latter being again subdivided, by allowing the trap to attain room temperature and collecting the gases evolved. The first two fractions were qualitatively almost identical for both esters, the more volatile consisting essentially of carbon monoxide, nitric oxide, methane, hydrogen and nitrogen, and the less volatile of acetaldehyde, methyl nitrite, carbon dioxide, nitrogen dioxide, nitrous oxide, ethylene, acetylene and hydrogen cyanide although acetylene was not observed with the 2,3-ester and methyl nitrite was not found in the products from the 1,4-ester. These two fractions were analysed quantitatively by a combination of i.r. and chemical techniques.

The liquid fraction was divided into three parts. Acids and aldehydes were determined by titration, and the remaining components were estimated i.r. spectroscopically both in methyl cyanide solution and in the vapour phase in a heated i.r. cell. Difficulties were encountered when nitrogen dioxide was present in the extracted flame samples. Some of this could not be evaporated from the liquid fraction and was estimated together with the organic acids by titration. Thus the curve labelled 'acids' in *Figure 8* is elevated at very short distances from the flame front ($< 1{\cdot}5$ mm) by the acids produced in the trap by the reaction of nitrogen dioxide with water and aldehydes. Infra-red spectra showed that the organic acids were mainly acetic acid in the case of the 2,3-BDDN and formic acid with the 1,4-BDDN, these being derived in all probability from oxidation by nitrogen dioxide of the aldehyde present in large quantities in the trap, i.e. from acetaldehyde (2,3-BDDN) or from formaldehyde (1,4-BDDN). Again, when nitrogen dioxide was present in the liquid fraction it seems that part of the aldehydes was polymerized to a material not reactive towards sodium sulphite. The polymer was identified as paraldehyde when acetaldehyde was a major ingredient of the liquid, but no positive identification could be made of the polymer from formaldehyde. From a comparison of the i.r. spectra of the liquid and that of a synthetic mixture of formaldehyde, formic acid and water, strong evidence could be obtained that the liquid fraction contained only these original ingredients. The small difference in weight between the sum of the analysed components and the total weight of the liquid fraction was assumed to be due to the polymer of the appropriate aldehyde. Total aldehyde only (as the monomer) is given in the product distribution curves.

Again, because of the reactivity of nitrogen dioxide, it is certain that the product samples analysed after condensation do not give a reliable indication of the amounts of nitrogen dioxide that were originally extracted from the flame. To obtain an estimate of the concentration of nitrogen dioxide in the flames an *in situ* absorption spectroscopic method was used.

A special water-cooled burner was designed so that first, a long absorpti path could be obtained and secondly, the difficulty of contaminated windo could be avoided. The burner is shown in *Figure 1*. It is made of copp

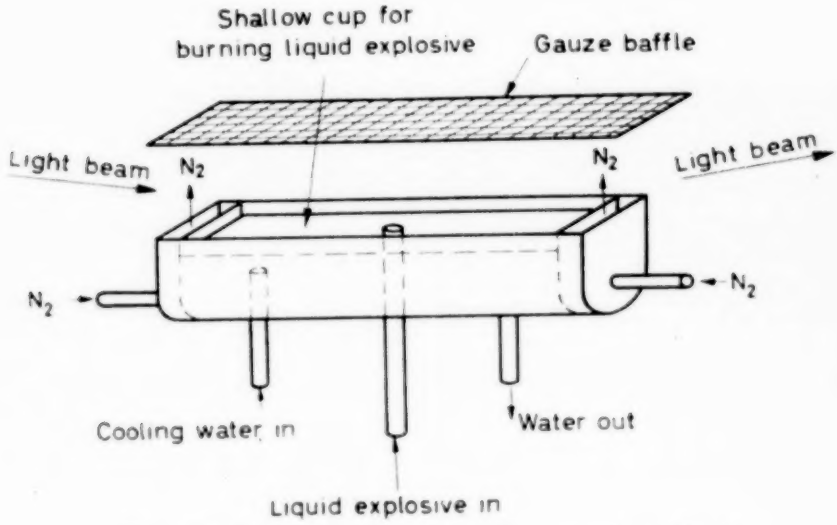


Figure 1. Burner for absorption spectroscopic methods

for rapid dissipation of heat and permits the liquid explosive to burn over a surface area of 10 cm by 1·7 cm in a shallow cup, the base of which is water-cooled. The products of reaction immediately above the liquid surface are allowed to burn in air at the side and the excess heat is removed through the burner. The diffusion flame is eliminated from the ends by a stream of nitrogen so that the scanning light beam does not pass through any flame other than the decomposition flame. The light source was either an ordinary tungsten filament lamp or a hydrogen arc lamp and a medium quartz spectrograph was used. A spectrogram, obtained by the usual method [see *Figure 2*(a)] of locating a vertical image of the spectrograph

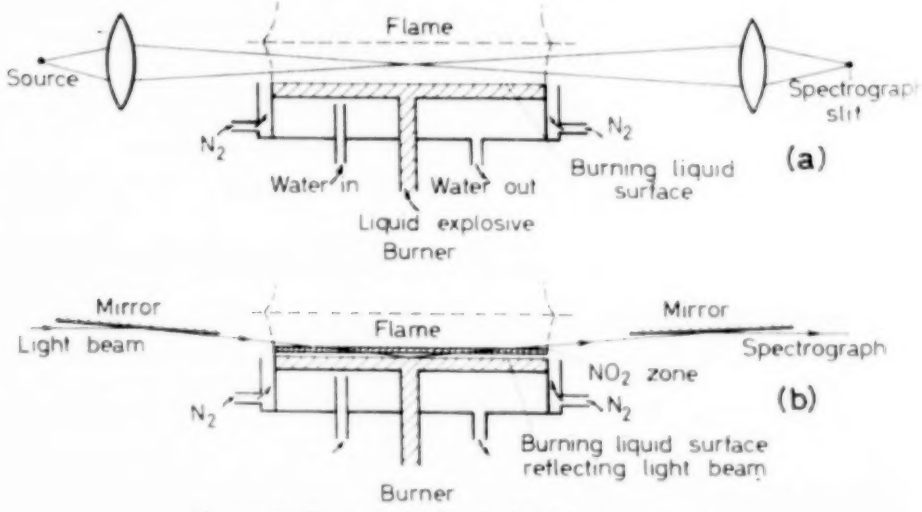


Figure 2. Two methods of obtaining spectrograms

slit the centre of the flame, is shown in *Figure 3*, and it reveals strong absorption by nitrogen dioxide in the early parts of the flame and some weak absorption throughout the flame. Refraction and reflections somewhat confuse the zone of the spectrogram in which the nitrogen dioxide absorption occurs, so a more positive technique for the estimation of the

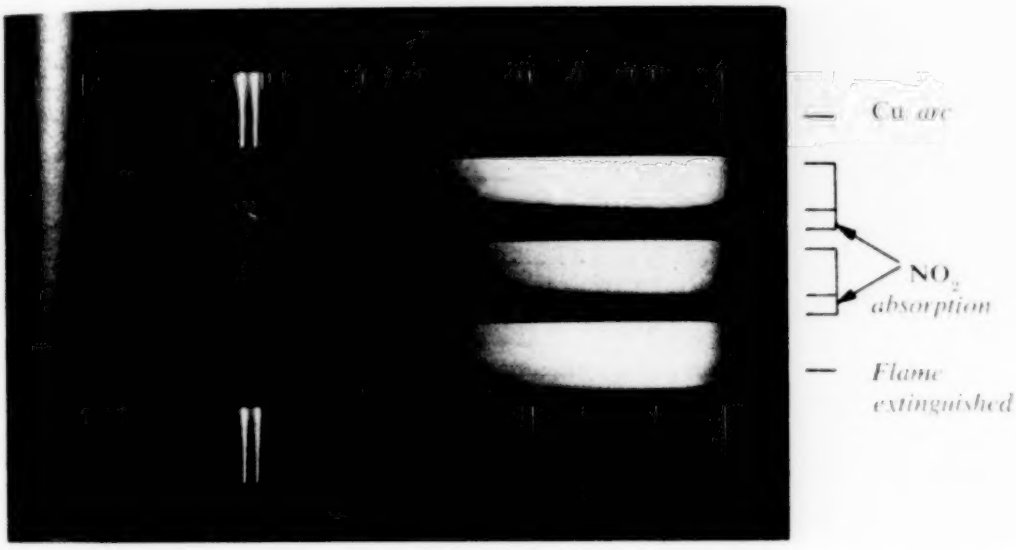


Figure 3. Absorption spectra of 2,3-BDDN flame using flat horizontal flame and vertical slit

concentration of nitrogen dioxide in the flame was developed. This entailed reflecting, at a narrow angle, the light beam off the burning liquid surface itself thus ensuring double passage of the beam through the narrow nitrogen dioxide zone. The method is represented diagrammatically in *Figure 2*(b). If some limits can be put on the thickness of the nitrogen dioxide zone, then the average concentration of nitrogen dioxide in the zone can be found by comparison of the optical densities of spectrograms of the flame with those of known pressures of nitrogen dioxide obtained under the same reflecting conditions but in the absence of the nitric ester flame. If the thickness of the nitrogen dioxide zone is taken to be 0·3 mm, which is an estimate from the analytical results and visual observation, and the temperature is taken to be 720° K, then an approximate value for the average concentration in the zone is 30 per cent by volume. The spectrograms taken by reflection are shown in *Figures 4*(b). It should be noted here that the ethyl nitrate flame showed no nitrogen dioxide by either method and the flames of the propyl nitrates only a trace on some, but not all, plates. The nitrogen dioxide values given in the figures are those obtained from analysis of extracted samples only and give a very low estimation of the amounts in the flame.

Rate of burning

The rates of burning of the liquid esters were determined at atmospheric pressure (in nitrogen) in a tube 24 mm in diameter, and for the 2,3-isomer

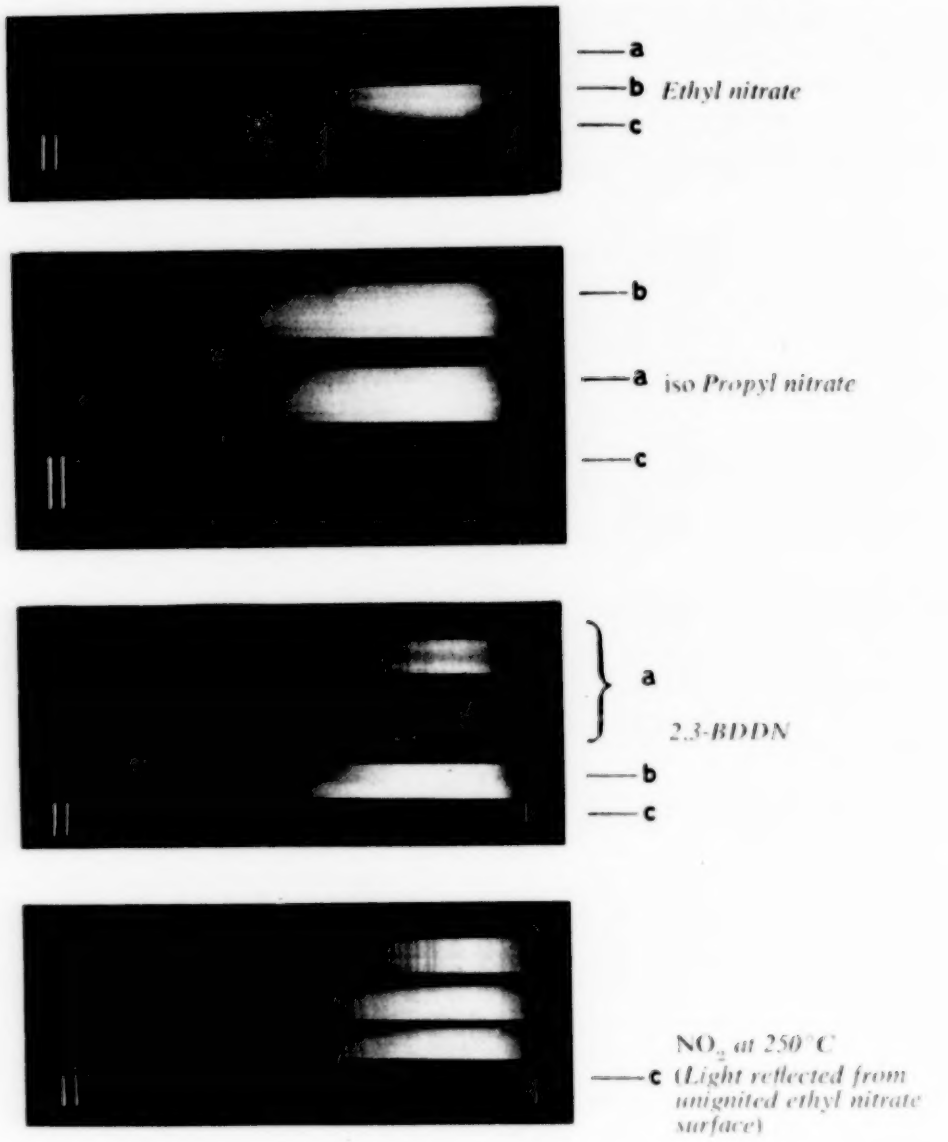


Figure 4. Absorption spectra of some nitric ester flames. (a) *Spectrum by reflection from burning liquid surfaces.* (b) *Spectrum by reflection from unignited liquid surface.* (c) *Copper arc*

the rates are compared with those of ethyl nitrate up to about 10^3 lb/in^2 in 5 mm tubes [see *Figure 5*]. At pressures approaching one atmosphere the rate depends very much on the experimental conditions.

The rates of burning of the two esters at atmospheric pressure under identical conditions were for 2,3-BDDN, 0·005 1 cm/s and for 1,4-BDDN, 0·003 5 cm/s. The rate of burning of ethyl nitrate (with a slightly lower heat of explosion) was 0·010 7 cm/s. Although in the 24 mm tube the 1,4-ester gave a lower rate than the 2,3-ester, in the flat flame burner the rate tended to increase over the long sampling period until it was faster than the 2,3-ester and almost as fast as ethyl nitrate. No similar increase in rate with time of burning was ever observed with the 2,3-BDDN.

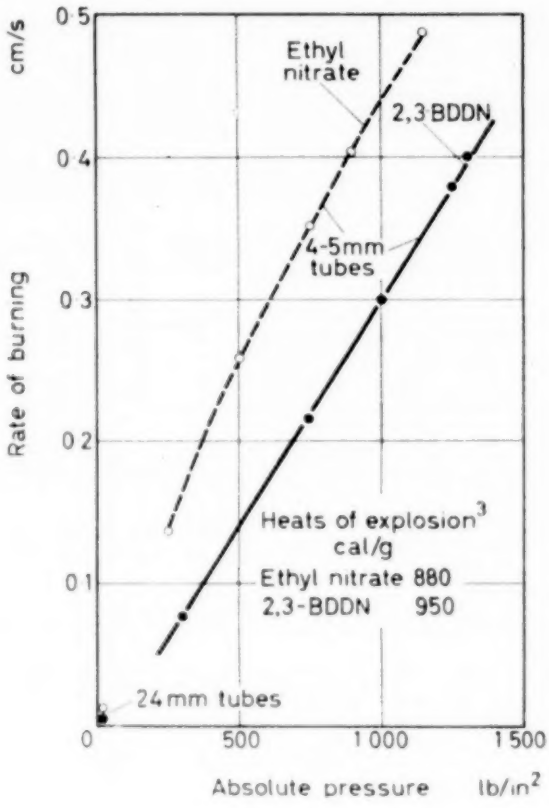


Figure 5. Rates of burning of liquid 2,3-BDDN

The burning velocities of some gaseous mixtures of nitrogen dioxide and acetaldehyde were determined in the flat flame burner. No special precautions were taken to obtain perfectly flat flames; therefore the values should be regarded as approximate. Maximum flame temperatures reached by these mixtures at atmospheric pressure were also determined using

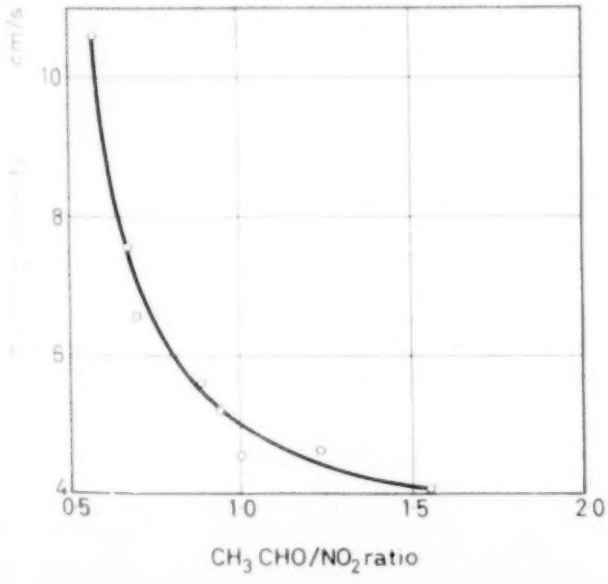


Figure 6. Burning velocity of upper limit acetaldehyde – nitrogen dioxide flames

covered Pt/Pt–Rh thermocouples. *Figure 6* gives the burning velocities of some upper limit mixtures of acetaldehyde and nitrogen dioxide and *Figure 7* their flame temperatures. The degree of preheat acquired by the gases in the burner was about 40°C.

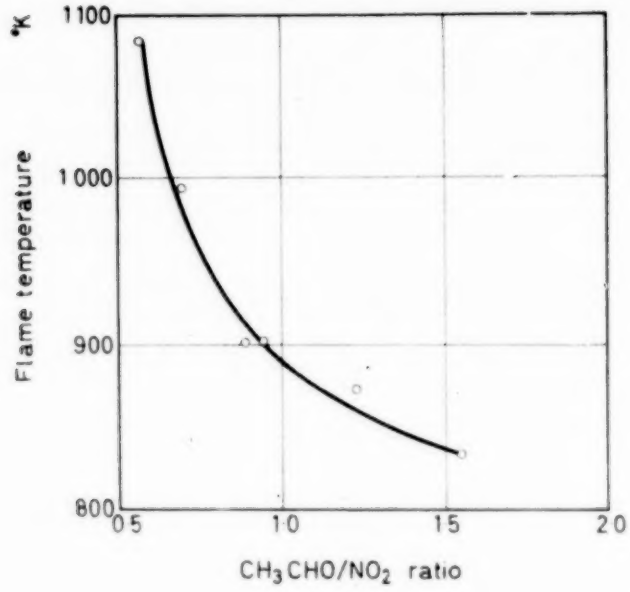


Figure 7. Flame temperatures of upper limit acetaldehyde–nitrogen dioxide flames

RESULTS

In *Figures 8* and 9, the number of moles of reaction product derived from 100 moles of 2,3-BDDN and 1,4-BDDN and the corresponding flame temperatures are plotted as a function of distance from the liquid surface upon which the flames were stabilized. As has been pointed out before, the nitrogen dioxide concentration in both flames is much higher than the gas samples would indicate; the concentration in the 2,3-BDDN was estimated spectroscopically to be about 30 per cent in the narrow zone shown on the temperature distribution curve. *Table 1* compares the products of the 2,3-BDDN flame with those of an acetaldehyde–nitrogen dioxide flame and *Table 2* the products of flames of 1,4-BDDN and formaldehyde–ethylene–nitrogen dioxide mixtures.

DISCUSSION

Decomposition mechanism of 2,3-BDDN

The important components in the samples extracted from this ester are nitric oxide, acetaldehyde, carbon monoxide and water vapour. There is spectroscopic evidence that the nitrogen dioxide is present in the flame in major quantities but undergoes extensive reduction to nitric oxide in the sampling process. Nitrogen dioxide and acetaldehyde, then, may be considered to be the main initial products with nitric oxide, carbon monoxide and water vapour as oxidation and decomposition products of reaction between them. There seems to be no evidence other than that this ester breaks down at the higher temperature in the simple manner assumed for most nitric esters in the low temperature range (~ 200°C).

The decomposition mechanism is exactly analogous to that of butane-2,3-diol dinitrite (~ 300°C), demonstrated by L. P. KUHN in his extensive work on dinitrites[1]. The overall decomposition of the 2,3-BDDN is

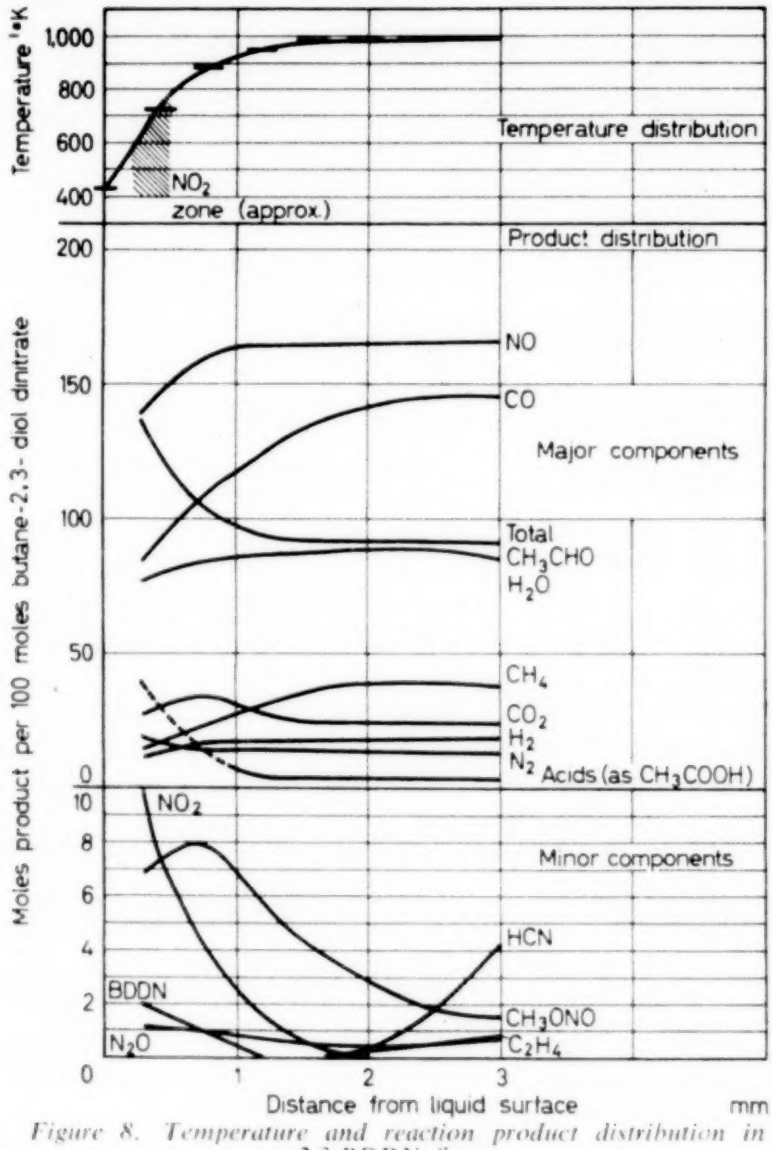


Figure 8. Temperature and reaction product distribution in 2,3-BDDN flame

described by reaction 1 which is endothermic by about 13 kcal/mole for liquid ester and gaseous products. This is in distinct contrast to the ethyl nitrate case[1] where the products of the flame decomposition could not be accounted for by the simple unimolecular decomposition.

$$\begin{array}{l} \mathrm{CH_3{-}CH(ONO_2){-}CH(ONO_2){-}CH_3} \longrightarrow 2\,\mathrm{CH_3CHO} + 2\,\mathrm{NO_2} \end{array} \qquad \ldots . [1]$$

The initial yield of acetaldehyde is 70 per cent of that expected from reaction 1 in spite of the fact that extensive oxidation of organic materials

by nitrogen dioxide has already taken place. It can be inferred that, once attack of acetaldehyde by nitrogen dioxide has taken place, oxidation of the fragments by nitrogen dioxide is more rapid than oxidation of other acetaldehyde molecules.

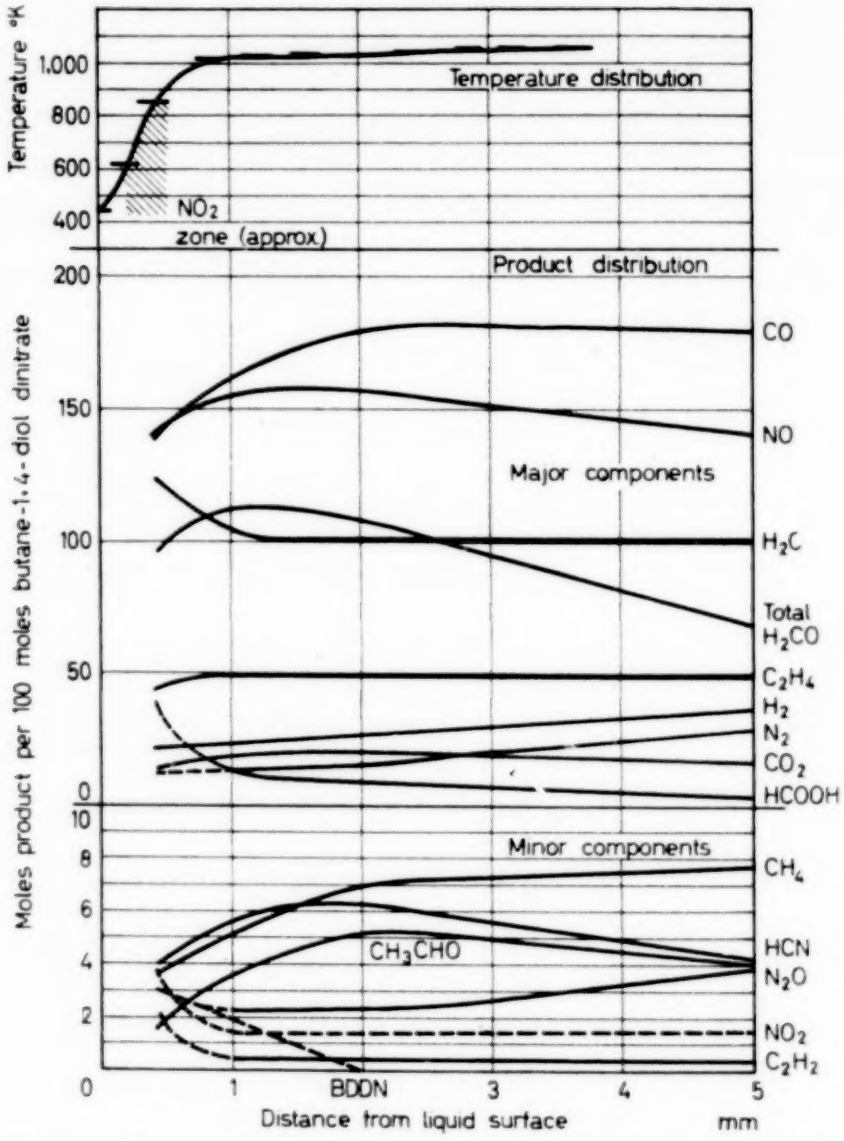


Figure 9. Temperature and reaction product distribution in 1,4-BDDN flame

If the primary decomposition of the 2,3-BDDN flame is in fact the result of an initial overall reaction according to reaction 1 then the products of final reaction would be expected to be identical with those of an equivalent synthetic mixture of nitrogen dioxide and acetaldehyde. (N.B. This evidence is only significant if the products are not in thermodynamic equilibrium.) The final products of the 2,3-BDDN are compared with those of two mixtures of nitrogen dioxide and acetaldehyde in *Table 1*. The $1\,NO_2 : 1\,CH_3CHO$ mixture would be expected to have a higher flame

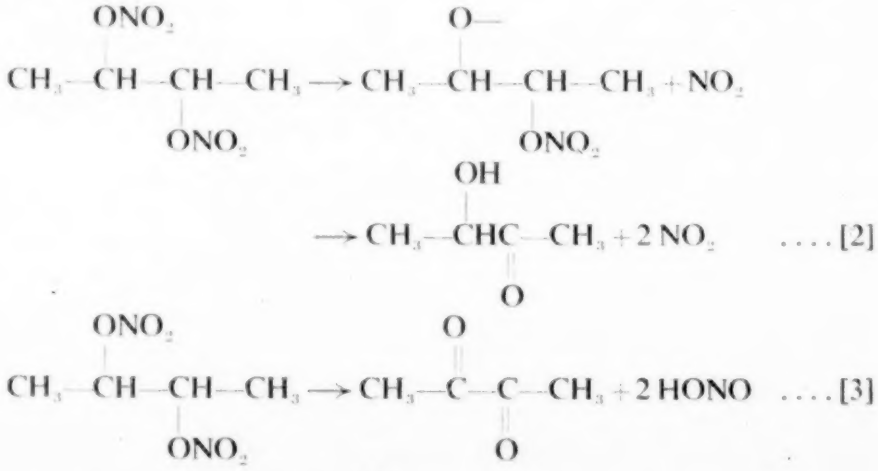
temperature than 2,3-BDDN because of the endothermicity of reaction 1, therefore a comparison with a 1 NO_2 : 1·44 CH_3CHO mixture, which is estimated to have about the same flame temperature, is also included. Allowance for the excess acetaldehyde and its decomposition products should be made in the latter case. Exactly the same products in approximately the same proportions are found in the 2,3-BDDN flame and the nitrogen dioxide–acetaldehyde flames. The observed flame temperature of the 1 NO_2 : 1·44 CH_3CHO mixture was in fact lower than that of 2,3-BDDN but their spatial burning velocities (i.e. burning velocities relative to stationary products) were almost exactly the same, namely 17 cm/s.

Table 1. Comparison of products from a 2,3-BDDN flame with those from premixed acetaldehyde–nitrogen dioxide flames

Component	*Moles product per 100 moles* NO_2		*Moles per 50 moles of 2,3-BDDN*
	1 NO_2 : 1·44 CH_3CHO*	1 NO_2 : 1 CH_3CHO†	
NO	90·3	81·2	76·5
H_2O	55·4	56·0	45·0
CO	78·4	77·3	63·0
CH_3CHO	78·6	30·5	41·5
CO_2	13·4	14·8	12·8
N_2	3·3	5·9	8·9
CH_4	27·3	31·4	19·0
H_2	3·3	9·9	3·4
CH_3ONO	1·8	0·6	2·5
N_2O	0·7	0·1	0·3
C_2H_4	0·2	0·9	0·3
Acids‡	2·2	0·9	1·4
CH_3OH	6·2	0·3	1·1
HCN	0·1	0·3	0·1

*Calculated to give approximately the same flame temperature as 2,3-BDDN.
†Same oxygen balance as 2,3-BDDN.
‡Estimated as acetic acid.

No trace of acetoin, $CH_3CH(OH)COCH_3$, or diacetyl, which might arise from reactions such as 2 and 3 below, could be found in the products from the nitric ester flame.



$$CH_3{-}CH(ONO_2){-}CH(ONO_2){-}CH_3 \rightarrow CH_3{-}C(=O){-}CH(ONO_2){-}CH_3 + NO_2$$

$$\rightarrow CH_3{-}C(=O){-}CH(OH){-}CH_3 + 2\,NO_2 \quad \ldots.[2]$$

$$CH_3{-}CH(ONO_2){-}CH(ONO_2){-}CH_3 \rightarrow CH_3{-}C(=O){-}C(=O){-}CH_3 + 2\,HONO \quad \ldots.[3]$$

When the disappearance of nitrogen dioxide is complete, little further reaction takes place in the products. The decomposition of acetaldehyde to carbon monoxide and methane is relatively slow. In fact, apart from the decomposition of the small amount of methyl nitrite produced in the early stages and the formation of small amounts of hydrogen cyanide and ethylene in the later stages of the flame, nothing more happens at atmospheric pressure. At higher pressures, of course, reaction between the fuel molecules and nitric oxide would become rapid and, at a sufficiently high pressure, appear as a secondary hot flame zone.

Decomposition mechanism of 1,4-BDDN

The major products of the initial decomposition of this ester are nitric oxide, carbon monoxide, formaldehyde, water vapour and ethylene. As for the 2,3-BDDN, a zone containing a higher concentration of nitrogen dioxide can be detected optically.

There is no evidence to suggest that the initial degradation of the ester takes place other than by fission of the weak —O—N— bonds and subsequent breakdown of the residue according to the overall reaction 4

$$\begin{array}{l} ONO_2 \\ | \\ CH_2—CH_2—CH_2—CH_2 \longrightarrow 2\,CH_2O + CH_2=CH_2 + 2\,NO_2 \quad \ldots . [4] \\ | \\ ONO_2 \end{array}$$

The heat of this reaction ($-\Delta H$) from liquid ester to gaseous products is −48·7 kcal. The final products of the flame are qualitatively identical with those from a synthetic formaldehyde–ethylene–nitrogen dioxide mixture. Again the exactly equivalent mixture $2\,NO_2 : 2\,H_2CO : 1\,C_2H_4$ gave a higher flame temperature than liquid 1,4-BDDN, so it was cooled with excess formaldehyde. The mixture having roughly the same flame temperature was

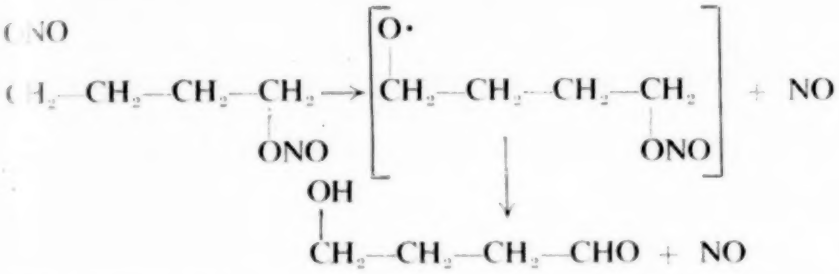
Table 2. Comparison of products from a 1,4-BDDN flame with those from a premixed formaldehyde ethylene nitrogen dioxide flame

Component	*Moles per 100 moles* NO_2 *in* $H_2CO\,C_2H_4\,NO_2$ *mixture**	*Moles per 50 moles of 1,4-BDDN*
NO	66·0	65·0
H_2O	84·0	48·0
CO	143·0†	86·0
CO_2	15·4	8·2
N_2	14·0	14·2
CH_4	6·8	3·8
H_2	50·7†	18·0
N_2O	1·8	2·0
C_2H_4	34·9	26·8
HCN	1·8	2·2
H_2CO	28·6	34·4
HCOOH	2·3	2·0
CH_3CHO	—	2·0
C_2H_2	0·9	0·2

*1 C_2H_4 : $2NO_2$: 3 $2H_2CO$.
†High values because of excess H_2CO added as coolant.

2 $NO_2 : 3{\cdot}2\,H_2CO : 1\,C_2H_4$, and is the mixture compared with the nitric e er in *Table 2*. In this case, when due allowance is made for the excess f maldehyde, the quantitative similarity is not so good.

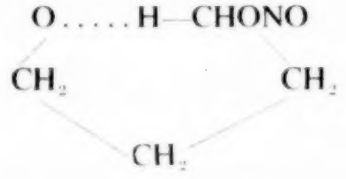
There is a significant difference between the flame decomposition of 1 -BDDN and the low temperature thermal decomposition of the dinitrite. I hn[4] finds that this dinitrite decomposes according to reaction 5.



$$\begin{array}{l} \text{(ONO} \\ \text{(H}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2 \rightarrow \end{array} \left[\begin{array}{l} \text{O}\cdot \\ \text{CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2 \\ \text{ONO} \end{array}\right] + \text{NO}$$

$$\begin{array}{l} \text{OH} \\ \text{CH}_2\text{—CH}_2\text{—CH}_2\text{—CHO} + \text{NO} \end{array} \qquad \ldots . [5]$$

This reaction involves an intra-molecular hydrogen transfer with the following cyclic transition state



It is reasonable to suppose that this type of rearrangement would be less likely in the high temperature decomposition of the dinitrate (taking place at around 800° to 900°K) than further direct breakdown to formaldehyde, ethylene and nitrogen dioxide.

Again, when nitrogen dioxide reactions are complete, little further reaction takes place at atmospheric pressure other than some continued reduction of nitric oxide linked with the decomposition of formaldehyde. This is considered later.

Some general considerations

The temperature gradient and the maximum temperature in the 1,4-ester re greater than those in the 2,3-ester, these observations being in line with he higher rate of burning of the 1,4-ester under our burner conditions. he maximum temperature reached at atmospheric pressure in both cases less than that for ethyl nitrate which has, in fact, a lower heat of explosion, t a higher rate of burning in narrow tubes. The initial gradient for the 4-BDDN can be equal to that of ethyl nitrate and, in fact, there is evidence at the rate of burning can approach that of ethyl nitrate in wide cups, if t in narrow tubes. The reason why this higher rate can be attained with e 1,4-BDDN and not the 2,3-BDDN is interesting but has not been rsued. The explanation of the lower flame temperature (N.B. at atmosheric pressure, thermodynamic equilibrium not attained) of these particular nitrates compared with ethyl nitrate lies in the greater reduction of nitric xide achieved in the latter and this also explains the higher temperatures the 1,4-BDDN flame relative to the 2,3-BDDN flame. 40 per cent is

reduced in the ethyl nitrate flame compared with 35 and 17 per cent respectively in the 1,4-BDDN and 2,3-BDDN flames. This reduction of nitric oxide is closely associated with the amount and rate of decomposition of the formaldehyde in the system. The curves for the rate of disappearance of nitric oxide and formaldehyde can be shown to be closely associated in several nitric ester decomposition flames in spite of a suggestion by A. R. HALL, J. C. MCCOUBREY and H. G. WOLFHARD[5] that formaldehyde is not involved in the reduction of nitric oxide. The significance of this relationship and the possible role of hydrogen atoms in the reduction of nitric oxide has been discussed in a separate study of the methyl nitrite flame[6] in which nitric oxide is extensively reduced by decomposing formaldehyde. With the two esters examined in this paper it can be seen that the ester which produces no formaldehyde in its decomposition (2,3-BDDN) has no ability to reduce nitric oxide beyond the flame front; the nitric oxide curve and the temperature curve are flat beyond about 1·5 mm (*Figure 8*). In the 1,4-ester, which produces almost as much formaldehyde as ethyl nitrate, reduction of nitric oxide continues beyond the flame front and there is a slow continual rise in the temperature curve. In the aldehyde–nitrogen dioxide mixtures, the flame of that containing formaldehyde shows a much greater reduction of nitric oxide to nitrogen.

From previous work in this programme on the effect of chemical structure on the flame decomposition of nitric esters, evidence has been presented to show that ethyl nitrate, *iso*propyl nitrate and *n*-propyl nitrate are destroyed by nitrogen dioxide and nitrous acid attack in a chain process. The stationary concentrations of nitrogen dioxide were too small to detect in these flames. It seemed possible that 2,3-BDDN and 1,4-BDDN might have a different mode of decomposition and this work attempts to show that these two esters do break down in flames in a unimolecular fashion and the exothermic reactions take place in the products of the early endothermic decomposition. High transient concentrations of nitrogen dioxide could be observed in the flame fronts.

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Waltham Abbey, Essex

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Investigations on the Inflammability Ranges of Methane–Air and Butane–Air Mixtures Ignited by Electric Sparks

GISÈLE DALMAI

A tentative explanation of the two-lobed shape of the inflammability ranges of a number of hydrocarbons is given in terms of the following sets of phenomena: (1) The apex lying between the two lobes is conditioned by flame quenching mainly caused by vibrations of the flame propagating inside a closed tube; (2) The 'second region' of the inflammability range is due to preferential diffusion of the deficient component of greater diffusivity. This causes a shifting of the mixture composition and leads to the propagation of small axial flames. This phenomenon occurs for mixtures richer than those determining the passage from one lobe to the other. At these concentrations the mixtures are considered 'at the limit'.

THE inflammability/propagability ranges (pressure/concentration) of combustible gaseous mixtures cannot be considered as characteristic of the mixture studied. They depend on other factors, such as the temperature at which the experiment is carried out, the direction of propagation, the geometry of the experimental vessel, ignition source, etc.

In particular, these mixtures ignited by a train of sparks instead of a single spark show a wider inflammability range divided into two lobes ('first region' and 'second region'). The flame types are different in each, the 'second region' is characterized by flames of the axial type[1–2].

The purpose of this study has been to determine the reason for the formation of these two lobes and to find out if it is merely an incidental phenomenon caused by the experimental conditions or if, on the contrary, it represents a property of the combustible mixture.

EXPERIMENTAL RESULTS

In order to determine the preponderance and interactions of the different factors which are likely to influence the inflammability ranges, we have studied these factors making use of statistical processes. These have shown that the diameter, the tube length and the electrode spacing play important roles in the propagation of flames in closed tubes[3].

Increasing both tube diameter and spark gap or decreasing the tube length tends to lower the critical pressure obtained especially for mixtures with partial propagation and flame quenching, i.e. mixtures giving rise to the characteristic two lobe range. The separation occurs at about 6·5 per cent for *n*-butane–air mixtures and 5·25 per cent for methane–air mixtures[4] (see *Figure 1* to *4*).

These factors may operate either through wall destruction or an alteration of the flow pattern of the burnt gases or even by variation of the initial volume ignited, and most probably through some combination of all three.

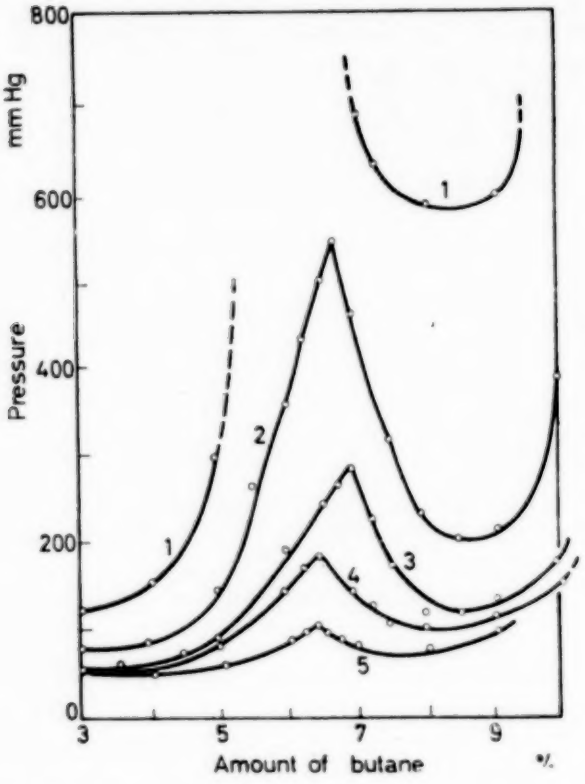

Figure 1. Influence of tube diameter on butane–air inflammability ranges. Diameters: curve 1—17 mm; 2—22·5 mm; 3—32·5 mm; 4—40 mm; 5—55 mm

Wall destruction

As we have shown[3] the inflammability ranges are independent of the nature of the vessel wall. The quenching of the flame for mixtures corresponding to the apex lying between the two lobes does not seem to result from the destruction of chain carriers on the wall surface.

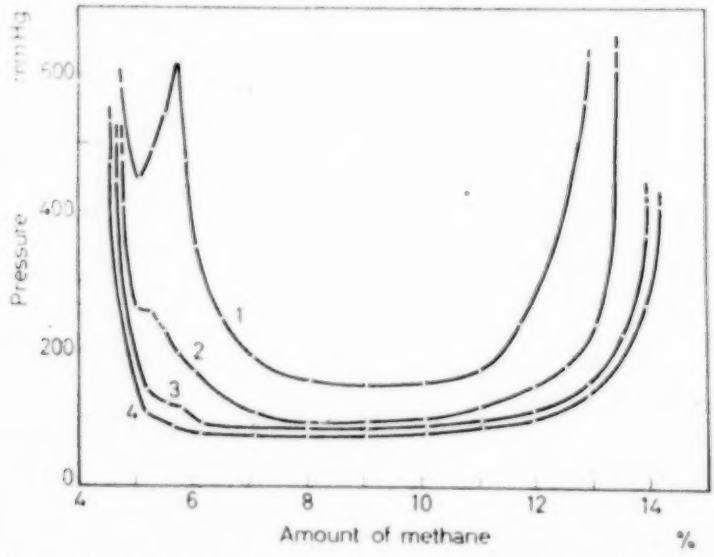

Figure 2. Influence of tube diameter on methane–air inflammability ranges. Diameters: curve 1—17 mm; 2—22·5 mm; 3—32·5 mm; 4—40 mm

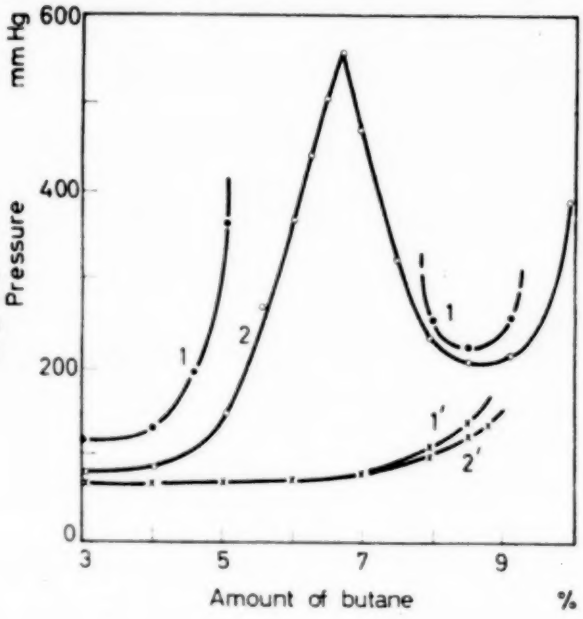

Figure 3. Influence of tube length on butane–air inflammability ranges. Length: 130 cm; diameter: curve 1—22·5 mm; 1'—70 mm. Length: 80 cm; diameter: curve 2—22·5 mm; 2'—70 mm

Burnt gases flow pattern

This quenching seems to be related to the flow pattern since by modifying the propagation regime through opening one end of the tube the shape of the inflammability ranges is altered. Indeed, when the tube is opened at the end of the ignition source, the flame vibrations are attenuated, the propagation which was partial becomes total and the inflammability range is no longer divided into two lobes (*Figure 5*).

In horizontal propagation, flames of the 'second region' are no longer observed, the convection probably upsetting the propagation of the flame (*Figure 5*).

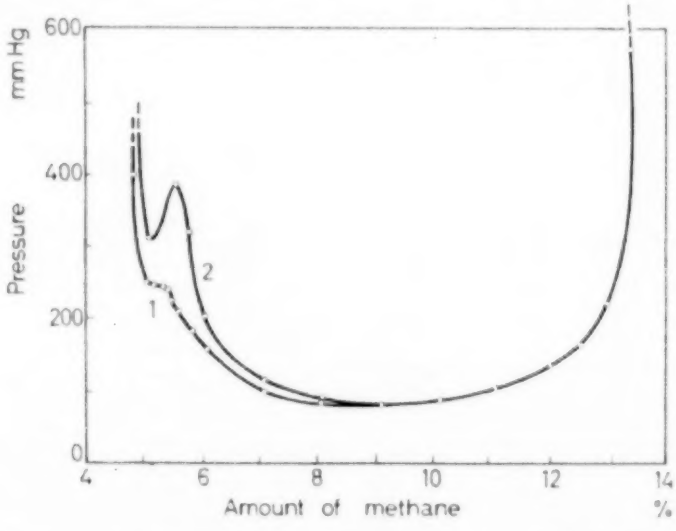

Figure 4. Influence of tube length on methane–air inflammability ranges. Length: 80 cm; diameter: curve 1—22·5 mm. Length: 130 cm; diameter: curve 2—22·5 mm

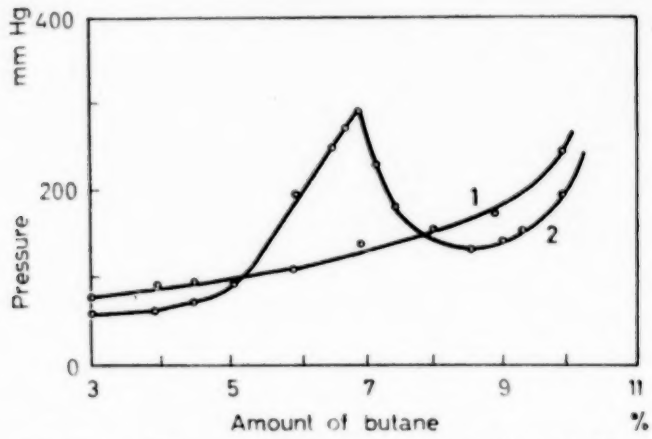

Figure 5. Curve 1—Tube opened at end of ignition source; 2—Closed tube

Initial ignited volume

The flame propagation is a function of the initial volume ignited in the zone of the electrodes[3–6]. According to the concentration and the nature of the initial mixture, the ignition will be isotropic or anisotropic. An isotropic ignition has been observed for *n*-butane–air rich mixtures and methane–air lean mixtures[7].

Anisotropic propagation (axial flames) has been observed by us for rich mixtures of butane and lean mixtures of methane.

Combustion products analysis

CO–CO_2—Gaseous products of combustion have been analysed by infrared spectrography. This has shown that the amount of carbon dioxide in the burnt gases passes through a maximum for the stoichiometric mixture whereas that of carbon monoxide is a minimum for this concentration. For

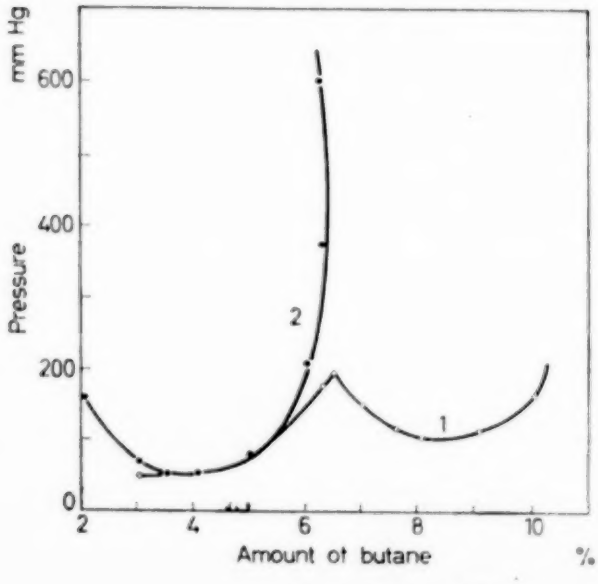

Figure 6. Curve 1—Vertical propagation; 2—Horizontal propagation

burnt gases of butane–air mixtures the amount of carbon monoxide decreases in the 'second region' (*Figures 7* and *8*). If we plot the ratio of the percentages of carbon monoxide and carbon dioxide against the initial

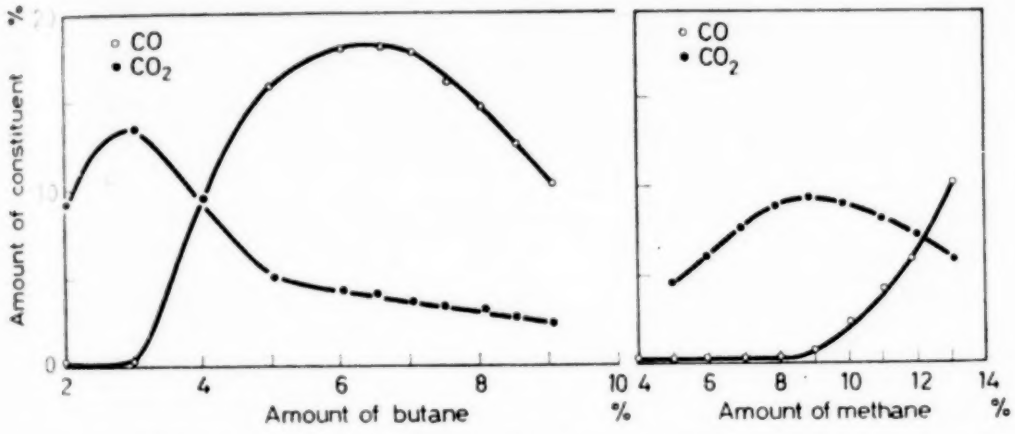

Figure 7. Amounts of carbon monoxide and carbon dioxide in combustion products of butane–air mixtures

Figure 8. Amounts of carbon monoxide and carbon dioxide in combustion products of methane–air mixtures

concentration of the hydrocarbons we notice that for butane–air mixtures these percentages increase up to about 7 per cent butane and then remain constant for the whole 'second region'. With methane–air mixtures, however, the ratio of carbon monoxide to carbon dioxide increases continuously up to the upper limit (*Figure 9*).

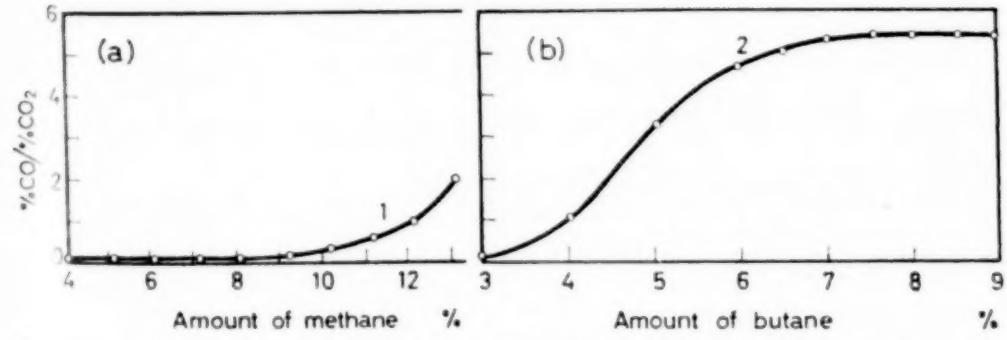

Figure 9. Ratio $\%CO/\%CO_2$. Curve 1—Methane–air mixtures; 2—Butane–air mixtures

H—As shown in *Figure 10* the concentration of butane in the burnt gases of *n*-butane–air mixtures is greater in the 'second region' than in the 'first'.

DISCUSSION

Bearing in mind that the flames of the 'second region' are quite different from those of the 'first region' since they occupy only the axial part of the vessel, we can imagine an effective central zone and a dead space between

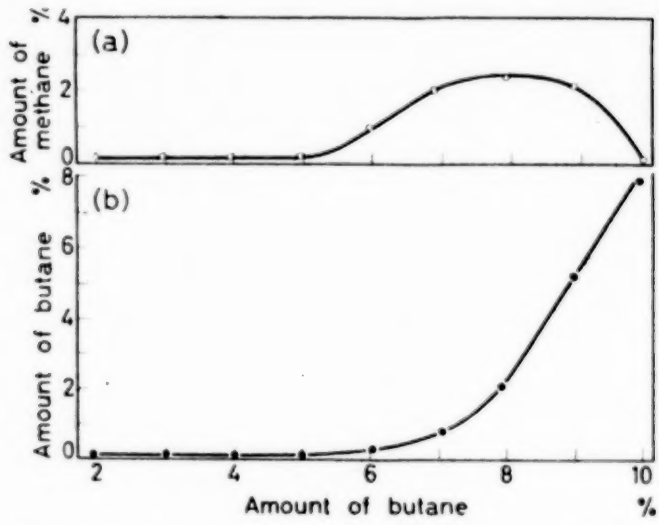

Figure 10. Amounts of methane and butane in combustion products of butane–air mixtures

the flame and the wall. In the dead space the temperature falls off rapidly. Carbon monoxide and carbon dioxide would be produced in the flame itself whereas peroxygenated products as well as most of the hydrocarbons found would originate from the dead space. These results explain the following points:

(*1*) The widening of the inflammability limits resulting from a train of sparks being used for ignition instead of a single spark—the axial type of the flame in the 'second region';

(*2*) The separation of the inflammability range into the two lobes.

(*1*) We believe that the widening of the inflammability limits and the axial type of the flames of the 'second region' depend on the initial ignited volume as well as the manner in which the energy is supplied to this volume.

Similar views have already been given by Markstein in explaining the structure of so-called cellular flames obtained for rich propane–air mixtures

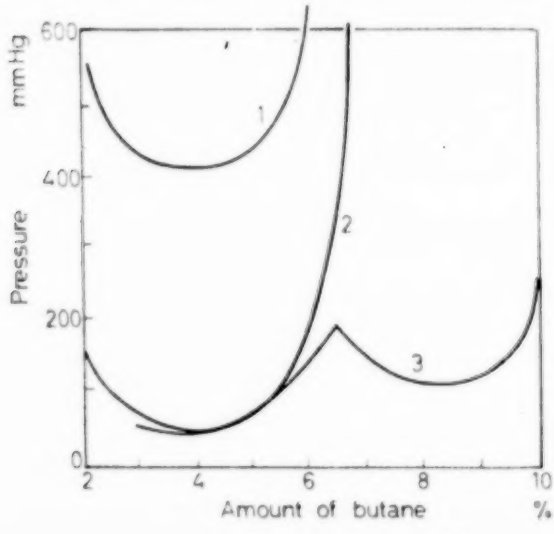

Figure 11. Effect of richer mixture with ignition by spark train compared with single spark ignition

together with a tentative explanation of the existence of anisotropic axial flames[8].

The reasons for the formation of cells in a flame leading to a cellular structure are not yet well established. It is, however, admitted that a limit mixture can become inflammable by the loss of only a small portion of either the combustible or the oxygen whichever is in excess. This shifting of the mixture composition can take place by differential diffusion of the component of greater diffusivity towards the central gaseous stream. This may lead to the axial flow falling inside the inflammability range and therefore to flame propagation. This preferential diffusion may have two causes:

(*a*) A thermal instability resulting from a non-continuous addition of energy;

(*b*) A concentration gradient favouring the diffusion of a component towards the flame in which it is being burnt.

It appears probable that, when a 'second region' is ignited by a single spark, preferential diffusion has insufficient time to become effective and the mixture does not ignite. However, during the passage of a train of sparks, the addition of energy is not only greater (lowering the pressure limit) but the time of passage is longer so that preferential diffusion of the component of lower concentration and of greater diffusivity may be established. The mixture concentration in the spark gap is therefore modified and it is likely to fall within the inflammability limits. Consequently the mixture becomes inflammable. The flame will then propagate anisotropically in the middle of the tube and the inflammability limits measured will be found larger.

If the inflammability limits of a combustible mixture are studied as a function of the source of ignition, it is to be expected that the greater the addition of energy, the larger the ranges obtained and the lower the pressure limits. If it is admitted that curve No. 1, *Figure 11*, corresponds to the *n*-butane–air inflammability range using a single spark, one may think that this range will become wider and that the pressure limits will be lower if ignition is brought about by a train of sparks. We have plotted a theoretical curve (No. 2, *Figure 11*) corresponding to the inflammability range obtained if the mixture is ignited by a train of sparks and if there were no preferential diffusion at the upper limit. If the experimental conditions are favourable to preferential diffusion it is to be expected that the inflammability limits will tend to widen even more. A new limit will be obtained at over-rich *n*-butane–air mixtures (curve No. 3, *Figure 11*).

A train of sparks seems to favour preferential diffusion as early as 6 per cent butane that is to say at the onset of the 'second range'. Thus the flame will burn in the 'first region' normally, occupying the whole section of the tube. Above 6·5 per cent in the initial volume of the spark gap, preferential diffusion takes place and ignition will occur in a mixture for which the concentration will be weaker. This will be followed by anisotropic propagation in a central gaseous stream. The true concentration of the mixture obtained by diffusion of the oxygen (butane–air mixture) must be at least equal to 6·5 per cent so that the flame can

propagate. It will be expected that the concentration of the gaseous central stream will always be equal to approximately 6·5 per cent in the whole of the 'second region' and a part of the hydrocarbons will remain unburnt in the dead space. As the initial concentration increases progressively in the 'second region' the section of the flame decreases and at a given concentration it requires such a large diffusion of oxygen that it is no longer consistent with the speed of energy dissipation provided by the spark. The central mixture will not be able to reach the concentration 6·5 per cent rapidly enough and flame propagation will not take place. This hypothesis is supported by the results of our experiments, as follows.

We have in fact only observed the formation of the 'second region' for those concentrations for which the deficient component is the most mobile, i.e. in rich butane–air mixtures and lean methane–air mixtures.

No 'second region' appears in horizontal propagation because convection interferes with anisotropic propagation.

The amounts of carbon monoxide and carbon dioxide decrease in the 'second region' whereas the ratio $\%CO/\%CO_2$ remains constant. In this region the amount of unburnt hydrocarbons increases.

If it is admitted that the carbon monoxide and carbon dioxide formed in the combustion products originate from the flame itself and that the hydrocarbon is unburnt in the dead space, an approximate calculation allows us to verify that the mixture which burns in the central stream in the 'second region' is roughly the 6·5 per cent mixture.

The thickness of a 9 per cent butane–air flame propagating in a 40 mm diameter tube is about 30 mm. It is observed that the amount of carbon monoxide and carbon dioxide found in a 9 per cent flame is equal to the calculated value of carbon monoxide and carbon dioxide formed in a flame of concentration equal to 6·5 per cent but occupying only about 9/16 of the tube cross section. We can see also that the amount of hydrocarbon (butane) remaining is equal to the sum of residual butane in a flame at 6·5 per cent occupying only 9/16 of the cross section of the tube and of the unburnt butane in the dead space. This is in good agreement with our assumption; however, it should be noticed that in the combustion products of a 'second region' flame not only does some of

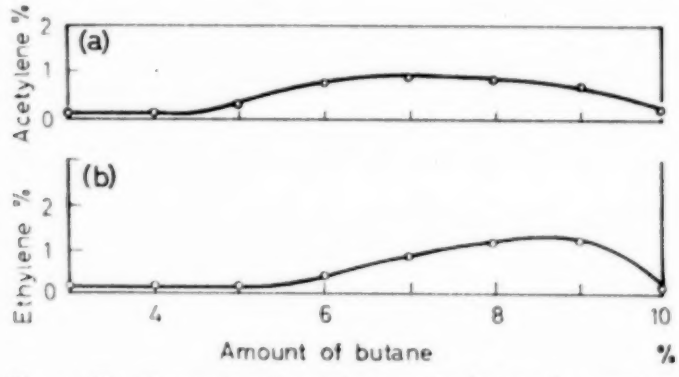

Figure 12. Amounts of acetylene and ethylene in combustion products of butane–air mixtures

the initial hydrocarbon remain unburnt but also saturated and unsaturated hydrocarbons originating from the pyrolysis of the initial hydrocarbon are found (*Figures 10* to *12*).

(c) In view of the above it can be legitimately considered that flames of mixtures whose concentrations lie close to that determining the passage from one lobe to the other (in fact situated at the apex of the low pressure range of these two-lobe curves) can be considered as limit flames which are actually those obtained when the ignition source and initial flame are such that no preferential diffusion can occur (curve No. 2, *Figure 11*). Obviously these flames are likely to be more easily disturbed than any stoichiometric mixture flame.

Considering now the two-lobe shape of the limit curves we must notice that H. GUÉNOCHE *et al.*[9] using Mallard et Le Chatelier recordings of propane–air flames propagating in a closed tube have established that flame propagation in the 'first region' is characterized by a sudden initial acceleration followed by a vibratory propagation whereas the 'second region' flames have a practically uniform movement. Furthermore, it is observed that there is no initial acceleration for the 'second region' flames.

With methane–air mixtures the propagation of flames of concentration near the upper limit is also characterized by an initial acceleration followed by a vibratory movement. It is to be noticed that green vibrating flames are observed both near the apex in the 'first region' of butane–air flames and near the upper limit for methane–air mixtures. Both by the recordings and by visual observation, it has been established that flame quenching at the upper limit of methane–air mixtures and at the end of the 'first region' of butane–air mixtures occurs when the flame is vibrating after the initial acceleration.

We presume that the flame is quenched in these vibrations owing to the fact that it is a flame near its limit and therefore easily disturbed.

This explains the partial propagation for pressures lower than the pressure limit with butane–air mixtures of concentration close to the one which determines the passage from one region to the other and with methane–air mixtures near the upper limit. During the passage of a train of sparks in a 'first region' mixture, a small gaseous volume is ignited in the electrode zone. This is followed by a three dimensional flame propagation. However, when the flame reaches the wall, the flame front area is cooled and reduced, so disturbing the gas flow. The reflected wave on the top of the tube causes the flame front to vibrate[8]. According to Guénoche's work it has been established that the vibration zone increases with the tube length but decreases when the gas flow conditions are modified. One can say that quenching will be more important with a long, narrow tube and that the pressure limits will be lowered when the tube is opened at the end of the ignition source. This is in good agreement with our experimental results.

The 'second region' flame does not vibrate and propagates uniformly in the tube. If one considers that these flames occur only when a preferential diffusion effect can be established one should expect that ignition will not take place instantaneously. Furthermore, the three dimensional flame

propagation will not reach the wall, the flame propagating in the mid[illegible] always remaining the same without flame front changes and therefo[illegible] without vibrations. Thus propagation in the 'second region' is slower a[illegible] more uniform.

Because quenching vibrations disappear in this region, it is normal to fi[illegible] lower pressure limits when the mixture strength is increased step by step [illegible] the 'second region'. However, above a given concentration the preferenti[illegible] diffusion occurs less readily and the flames no longer propagate: the upp[illegible] limit is said to be reached.

CONCLUSION

In conclusion it may be said that the nature of the low pressure curve of the inflammability ranges considered seems mainly due to factors conditioning the quenching of a propagating flame. Vibrations in closed tubes are amongst the most important factors leading to the arrest of such propagation.

The fact that the so-called 'second region' extends well outside the limits of inflammability and is characterized by a particular type of flame (axial flame) is satisfactorily interpreted in terms of a preferential diffusion of the deficient component of greater diffusivity. All the flames encountered beyond the apex of the low pressure curve can be considered as limit flames.

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Gaseous Nitric Acid–Hydrocarbon Flames

J. MERTENS and R. L. POTTER

Burning velocities of gaseous nitric acid and four hydrocarbons, propane, n-heptane, methylcyclopentane, and toluene have been measured at atmospheric pressure. Burning velocities of nitric acid–propane flames also have been measured at a half and two atmospheres. Flame temperature measurements and spectroscopic observations have been made for some of these flames. The appearance of these flames is similar to hydrocarbon flames burning with nitrogen dioxide; however, the second combustion wave does not appear unless piloted by secondary air when the temperature of the combustible mixture is 400° K. When the temperature of the combustible mixture is raised so that the final adiabatic flame temperature approaches 3,000° K, reactions downstream of the first combustion wave are speeded up sufficiently to produce a new combustion wave in the absence of secondary air.

THE combustion behaviour of oxidizers other than oxygen with various fuels has recently become of widespread interest. Among the more important ones that have been studied are the oxides of nitrogen. They have been the subject of numerous investigations by many workers[1–5]. Hydrocarbon flames supported by another nitrogen-containing oxidizer, gaseous nitric acid, have been investigated by M. H. BOYER and P. E. FRIEBERTSHAUSER[6]. R. L. POTTER and co-workers[7–9] have also reported the detonation characteristics of gaseous nitric acid–hydrocarbon mixtures, including detonatability limits. Common to all these studies is the curious fact that nitric oxide, an intermediate in the reduction of the higher oxides and nitric acid, is a reluctant oxidizer despite its thermodynamic instability. A general qualitative picture of the role played by nitric oxide in flames has been given by H. G. WOLFHARD and others[1, 2, 5].

In an effort to accumulate more information concerning the combustion characteristics of nitric acid–hydrocarbon mixtures, measurements of the laminar burning velocities and temperatures have been made. Also some spectroscopic observations have been made and are reported. It is felt that the combustion behaviour of these mixtures, including the short 'run-distance' characteristic of nitric acid–hydrocarbon detonations and their detonation limits will be within reach of theoretical analysis when sufficient data of this nature are available. On the basis of results reported here, the inferences by H. G. Wolfhard concerning the role played by nitric oxide in flames are further supported.

EXPERIMENTAL PROCEDURE

The oxidizer used in these experiments was nitric acid, purchased from General Chemical Company in accordance with Specification *MIL–N–7254B* (USAF) Type I. This acid was about 97·5 weight per cent HNO_3, the remainder being water and nitrogen dioxide. In the majority of experiments this acid was used without any attempt at purification because it was found

that distilled acid having better than 99·5 weight per cent purity did no give vaporized acid compositions sensibly different from the purchase acid. The hydrocarbons, *n*-heptane, methyl*cyclo*pentane, and toluene wer Phillips Petroleum 'Pure' grade; the propane was from The Matheso Company; all these were used without purification.

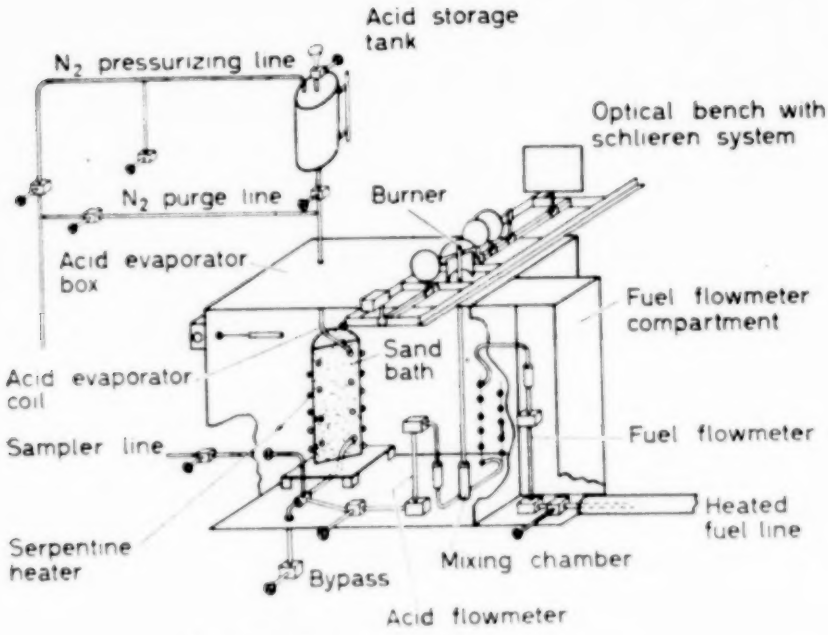


Figure 1. Burner and evaporating system

A schematic diagram of the apparatus used is shown in *Figure 1*. The nitric acid was forced under pressure through an aluminium evaporating coil set in a heated sand bath. The box containing valves, tubes, check valves, and flowmeters, etc. was insulated and thermostatted. Fischer–Porter Flowrators were used to meter the flows; a sapphire float was used on the acid side. The acid flowmeter was calibrated at atmospheric pressure by flowing vapours through it, condensing and weighing the acid. A value of the viscosity of acid vapour of 150 micropoise at 400°K was estimated from the critical constants[10]; using this, and the Fischer–Porter charts, a calibration curve was drawn which agreed almost exactly with the experimental calibration curve. The acid was analysed and it averaged about 96 weight per cent HNO_3, the balance being water and nitrogen dioxide. Because of decomposition, some oxygen must be evolved; this was estimated by a mole balance. The average acid vapour composition, in mole per cent, was: HNO_3—91·0, NO_2—3·20, H_2O—4·34, O_2—1·49. Because of the excellent agreement between the experimental and calculated calibration curves obtained at one atmosphere, calculated calibration curves were used at a half and two atmospheres. A bypass line, just upstream of the acid flowmeter, allowed continuous sampling of the acid vapour while experiments were being carried out. The calculated volume flow took into account the slight reduction in molecular weight due to the acid dissociation

The temperature of the combustible gas mixture was 400° K in all cases except for a few experiments mentioned later.

Vaporized fuel entered the thermostatted box, flowed through an aluminium coil to achieve temperature equilibration and thence through a flowmeter to the mixing chamber. The temperature of the gas mixture was measured in the mixing chamber by means of a shielded thermocouple. The combustible gas mixture passed from the mixing chamber up the burner tube which was made of Pyrex. The outside of the glass tube was wound with resistance wire and the whole tube could be heated throughout its length. A thermocouple at the burner tip provided information about the temperature difference between tip and mixing chamber, and heat could be applied by means of the resistance wire to the burner tube so that a negligible temperature gradient existed. A surrounding concentric tube allowed a nitrogen shield to be placed around the flame. A sturdily constructed pressure chamber was used for work at other than atmospheric pressure. A special electrically heated superheater was used to provide combustible gas temperatures higher than 400° K.

The Pyrex burner tubes were all 50 cm long. The diameters were small, being 0·12 cm at two atmospheres, 0·16 cm at one atmosphere, and 0·239 cm at a half atmosphere. Only with such small burners could laminar flames be maintained over the entire mixture range without flashback occurring. We do not know what the quenching distance is for these flames; however, 'detonative' flashback occurred several times in a slot-burner less than 0·25 mm × 12 mm. Using estimated viscosities, Reynolds numbers were calculated for the various conditions; the maximum Reynolds number for the half atmosphere work was 1 000, for one atmosphere—1 800, and for two atmospheres—2 000. The image of the flame was obtained by a straight-through schlieren apparatus with a magnification of about three.

APPEARANCE OF FLAMES

The qualitative description of the flames agrees in the case of the aliphatic hydrocarbon fuels with that given by M. H. Boyer and P. E. Frieberts-hauser[6]. The unburnt gases first pass through a combustion wave that changes from purple on the fuel-rich side to orange on the acid-rich side. The behaviour of this first wave does not appear to be influenced by the surrounding medium. The succeeding behaviour of the gases downstream of this wave is influenced by the surroundings, however. In the presence of a nitrogen mantle, nothing is seen above this first wave. In the presence of air, an outer mantle develops which changes character with mixture strength. This outer mantle can also be eliminated by a Smithells separator. With a Smithells separator of 3·75 cm diameter, the outer mantle could be stabilized at the top, or it could be extinguished, depending on the flow of combustible mixture. The outer mantle consists of a thin blue–grey zone followed by a doublet of two different pinks. This is followed in turn by another blue zone and finally by a yellow–orange zone. At mixtures corresponding to the maximum burning velocity, the blue–grey zone appears to vanish into the first combustion wave. On moving farther into the

acid-rich mixtures, the outer mantle lifts off gradually, leaving behind th orange inner combustion wave.

While methyl*cyclo*pentane behaved like the aliphatic hydrocarbon toluene, the aromatic representative behaved differently in the fuel-ric mixtures. In secondary air, the fuel-rich nitric acid–toluene flame was a brilliant, if not more so, than an oxyacetylene flame. This brilliant whit flame was due to atmospheric oxygen reacting with the gases downstrea of the first combustion wave, as could be shown by substituting nitroge for air around the flame. When this was done, the first combustion wav alone was left.

The schlieren images of the inner combustion wave, or cone, were shar and clear at pressures of two and one atmospheres and were slightly less so at a half atmosphere. This behaviour is to be expected since the reaction zone increases in thickness with decreasing pressure. Thus as the pressure decreases, the density gradient across the reaction zone decreases. Also of interest is the observation that over the fourfold pressure range investigated, there was no evidence that the reactions in the burnt gas above the first cone were speeding up. This was apparent because the outer mantle showed no shift in position with increasing pressure when the flame burned in secondary air. The outer mantle was diffuse as no schlieren image could be obtained. It was easy to distinguish between laminar and turbulent flow conditions, as under the former circumstances the tip of the cone was sharp and clear. When the approach flow was turbulent the tip opened up.

Some additional experiments with acid and propane were performed at atmospheric pressure in which the initial temperature was raised above 600°K. The acid composition was not measured in these experiments. These flames showed marked differences from the other flames. In particular, in experiments carried out in a Smithells separator, it was clear that the reactions in the gases downstream of the first combustion wave were speeding up. In fact, a new wave that was independent of secondary air, blue in colour, formed just downstream of the first wave.

BURNING VELOCITIES

The flame velocities were determined by the total area method. Sever other methods were tried but the scatter of results indicates that suc refinements were unwarranted in the present experiments. The inner co was used to define the flame area. The burning velocities reported we all obtained in secondary air, as air was demonstrated to have no influen on the inner combustion wave. The burning velocity results for all fo hydrocarbons, propane, *n*-heptane, methyl*cyclo*pentane, and toluene at o atmosphere pressure are shown in *Figure 2*. The results for propane an *n*-heptane at a half atmosphere are shown in *Figure 3*. Those for propan at two atmospheres are shown in *Figure 4*, and finally in *Figure 5* th results for propane at all three pressures are collected together. Fro the results of *Figure 2* it can be seen that the maxima in the burnin velocities all occur on the oxidizer-rich side of stoichiometric (stoichiometri

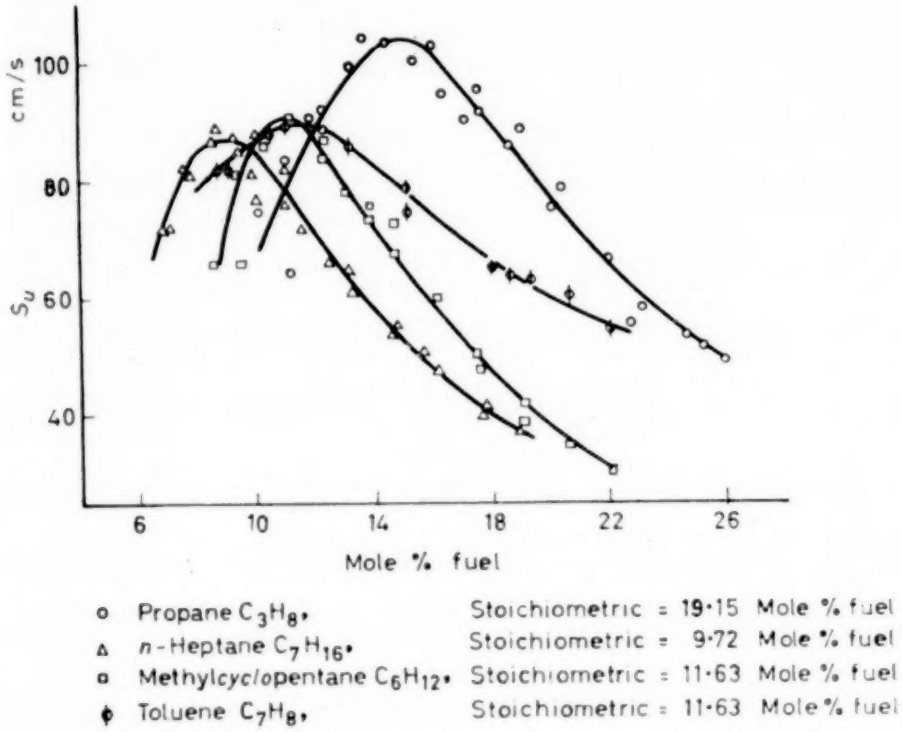


Figure 2. Burning velocities of nitric acid–hydrocarbon flames at 1 atm and 400° K

being defined as that mixture which gives for products of combustion carbon dioxide, water vapour, and nitrogen). When using volume per cent compositions, stoichiometric depends on the acid composition; stoichiometric compositions were calculated using the acid composition used in the volume flow calculations. It is also of interest to note that the burning velocity decreases as the molecular weight of the fuel increases. With propane there is a definite shift of the maximum in burning velocities toward stoichiometric mixtures as the pressure is increased. Our results for acid and propane are higher than those reported by M. H. BOYER and P. E.

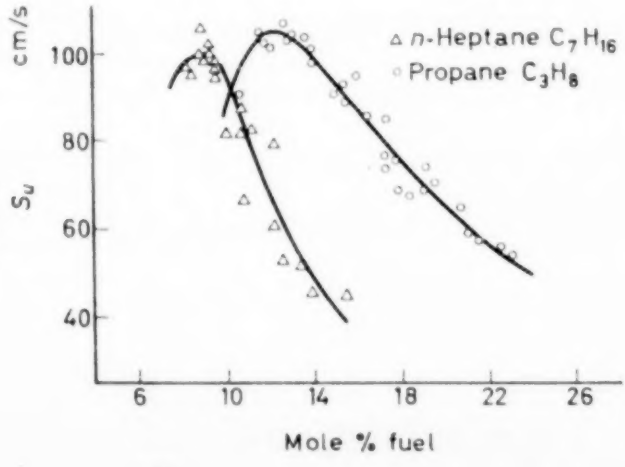


Figure 3. Burning velocities of nitric acid–hydrocarbon flames at 0·5 atm and 400° K

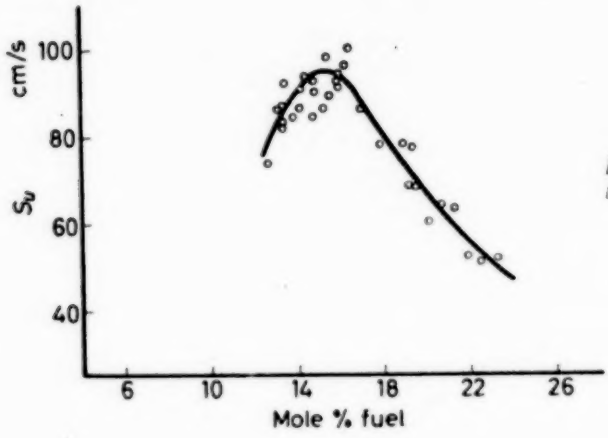


Figure 4. Burning velocities of nitric acid–propane flame at 2 atm and 400° K

FRIEBERTSHAUSER[6]; however, it is believed the data presented herein are correct to a few cm/s. The absolute error may be larger because of the small burners used; however, the trends exhibited should be correct. The experiments at two atmospheres were most difficult, as the temperature required to prevent condensation was beyond the limits of our apparatus when the higher boiling hydrocarbons were used. Some results were obtained with *n*-heptane but they are of much lower quality than those with propane and so are not reported. The decrease in burning velocity of the nitric acid–propane mixture at two atmospheres from that at the lower pressures may well be due to experimental error in determining the area of the flame, the flow measurements, and the small size of burner required to prevent flashback. At any rate, the pressure dependence of the burning velocity within the range investigated is obviously small for propane, while for *n*-heptane the burning velocity increases with decreasing pressure.

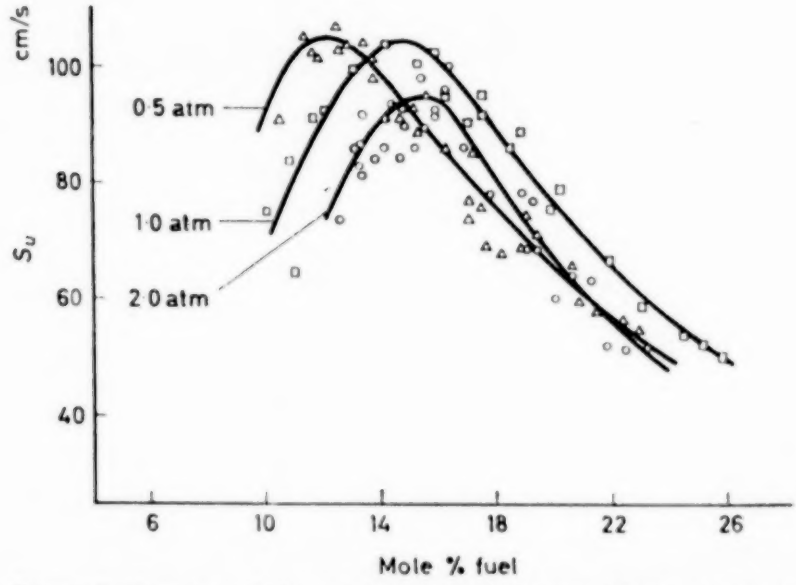


Figure 5. Burning velocities of nitric acid–propane flames at 0·5, 1 and 2 atm and 400° K

FLAME TEMPERATURE

Flame temperature measurements are important, especially in multistage flames, as quantitative information about the progress of combustion at each stage is obtained. The flame temperatures of nitric acid–propane flames in air were measured by the conventional sodium line-reversal technique. These temperatures are for a zone 2 mm above the inner cone and below the second combustion wave. The measured values of the temperature, as a function of mixture strength are shown in *Figure 6*. Including sources of error due to fluctuating mixture strength during measurements, calibration errors, etc., it is estimated that these temperatures are correct to $\pm 30^{\circ}$C. This is sufficient for our purpose. The theoretical flame temperatures for these mixtures, assuming thermodynamic equilibrium in the burnt gases, are also shown for comparison in *Figure 6*. These were

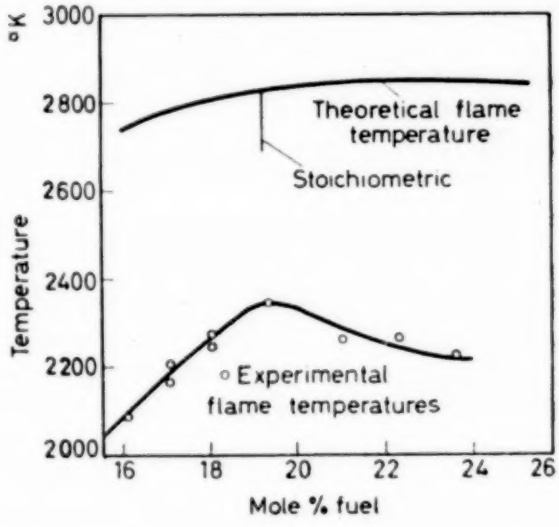


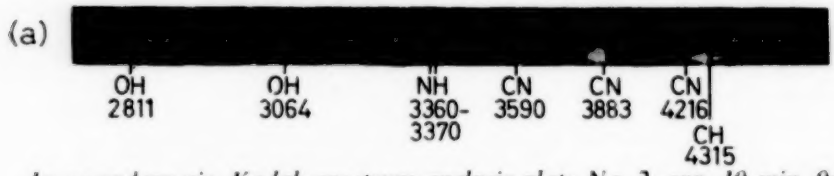
Figure 6. Nitric acid–propane flame temperatures (burning in secondary air, 2 mm above inner cone)

calculated on an IBM–650 digital computer. As is to be expected, the temperature over the inner cone is not the final flame temperature, this would only be reached at the last stage in a multistage flame. Some computations were made to discover what flame temperature would be attained if the acid was reduced solely to nitric oxide. For example, at a mixture strength of 19·3 mole per cent propane the temperature comes out to be about 1 670°K, which is far below the observed temperature. If 26 mole per cent of the nitric oxide decomposes to nitrogen, however, the calculated flame temperature is brought up to the observed temperature of 2 340°K the remaining products are distributed according to thermodynamic equilibrium. Partial conversion of the nitric oxide on passing through the first combustion wave is reported by M. H. BOYER and P. E. FRIEBERTSHAUSER[6]; however, they give no results for nitric acid–propane.

SPECTROSCOPIC INVESTIGATION

The radiation emitted from a flame offers further means of elucidating the complex reactions taking place. Hence spectroscopic investigations of the radiation emitted and absorbed by nitric acid–hydrocarbon flames were

carried out in the violet and ultra-violet regions. For this purpose a Hilger Medium Quartz Spectrograph was used. Further accessories used included quartz lenses and a hydrogen discharge tube which was used for absorption studies in the ultra-violet. The plates used were Eastman Kodak Spectrum Analysis Plates No. 2 and Spectroscopic Plates No. 103–F. A special slot burner was used having dimensions 0·25 mm × 10 mm, and the flames were viewed along the long dimension of the burner. The burner was equipped with an annulus so that a nitrogen envelope could be provided. The burner height was adjustable so that traverses could be made at different heights above the top of the burner.



In secondary air. Kodak spectrum analysis plate No. 2. exp. 10 min. 0·03 mm slit

In secondary nitrogen. Kodak spectrum analysis plate No. 2. exp. 10 min. 0·02 mm slit

In secondary nitrogen. Kodak spectroscopic plate No. 103-F3. exp. 5 min. 0·025 mm slit

Figure 7. Emission spectra of inner cone of a nitric acid–propane flame at 16 mole per cent C_3H_8

Emission spectra of an acid-rich nitric acid–propane flame are shown in *Figure 7*, (a) being in air and (b) and (c) in secondary nitrogen. In both cases the inner cone was focused on the slit of the spectrograph. Plates having different spectral sensitivities were used, this accounting for some of the differences. The most striking difference is the occurrence of OH bands in the flames surrounded by air and their non-occurrence when the flame is surrounded by nitrogen. The continuum from 6 500Å to 5 000Å is probably indicative of the reaction[11]

$$NO + O = NO_2 + h\nu$$

The NH band at 3 360Å shows up in both cases. CN and CH bands also occur in both cases. Emission spectra taken above the inner cone in secondary air revealed strong OH bands and CN bands while in secondary nitrogen no emission from the hot gases was recorded. Spectra of nitric acid–toluene, and *n*-heptane flames in air showed no striking differences from the nitric acid–propane flame.

While NO γ-bands showed in emission, they were so weak they could not be reproduced. However, the NO γ-bands showed up strongly in absorption in secondary air and in secondary nitrogen. The OH bands

did not appear in absorption, even in secondary air. In one case (at about 16 mole per cent propane), the NO γ-bands were followed in absorption at least 3 cm above the inner cone when the flame was surrounded by secondary nitrogen. According to microdensitometer readings of the plate, the absorption stayed nearly constant, implying that very little conversion of the nitric oxide took place in the gases above the inner cone. When air was substituted for secondary nitrogen around the flame, the NO absorption bands nearly disappeared by the time the top of the outer flame mantle was reached, implying that when nitric acid–propane flames burn in secondary air, the nitric oxide is almost completely converted to nitrogen.

DISCUSSION OF RESULTS

The experimental results of the flame speeds of gaseous nitric acid and several hydrocarbons, the flame temperature measurements, as well as the spectroscopic observations, constitute a considerable amount of information concerning the combustion characteristics of nitric acid. It is the formation of nitric oxide in the first combustion wave that is responsible for the distinctive appearance of these flames just as it is in the case of nitrogen dioxide supported flames where multistage flames are also observed. As a result of the observed flame temperatures over the inner cone coupled with the compositions required to give equivalent temperatures, as well as the direct observations of the conversion of the nitrogen in nitric acid to nitric oxide, it is clear that the conversion of nitric acid to nitric oxide is not quantitative in passing through the inner cone. This nitric oxide in the gases downstream of the first combustion wave is practically inert. For example, in the absence of secondary air, at 16 mole per cent propane where the observed flame temperature is about 2 100° K, and using the kinetic data of H. WISE and M. F. FRECH[12] for the homogeneous, bimolecular decomposition rate of nitric oxide, calculations for the flow system predict that only 20 per cent of the nitric oxide will be converted in a distance of 3 cm downstream of the first combustion wave. Absorption experiments confirm that very little conversion of nitric oxide takes place under these circumstances. Even with long exposures, no radical emission was observed above the inner cone, in flames surrounded by secondary nitrogen, indicating the absence of appreciable quantities of these species. Hence the decomposition of nitric oxide in the absence of air over the inner cone may confidently be assumed thermal in nature.

When the flame burns in secondary air, the nitric oxide absorption ceases above the outer flame zone. The emission spectrum above the inner cone in secondary air is very rich in radical emission, especially OH, CN, some CH and very small amounts of NH. There appear to be some β bands of CO also. All this emission is much less intense on the oxidizer-rich side than on the fuel-rich side. Although it is clear that the temperature of the gas above the inner cone must rise due to reaction of atmospheric oxygen with the incompletely reacted fuel, and that this fact could account for the observed removal of nitric oxide, it is also possible to ascribe the enhanced decomposition rate to reactions with radicals.

Leaving for a moment the reactions in the gases above the inner cone, consider the evidence concerning the inner cone itself. From observations previously presented, some of the nitrogen in the nitric acid is completely reduced to molecular nitrogen, while the majority passes out on the downstream side of the first combustion wave combined with oxygen as nitric oxide. The idea that all the nitrogen is first converted to nitric oxide followed by partial decomposition by thermal routes alone can be rejected because there is not enough time during passage through the thin combustion wave (estimated to be less than 0·1 mm at atmospheric pressure) to decompose measurable quantities of the nitric oxide. Experimental absorption data support the correctness of the kinetic data upon which this statement is founded. As mentioned before, absorption measurements showed no appreciable decomposition in a nitrogen-shielded flame for distances of 300 times the thickness of the flame zone and under circumstances where the average temperature was identical to the final temperature of the inner cone. D. P. NEEDHAM and J. POWLING[13, 14] have drawn similar conclusions for ethyl and propyl nitrate decomposition flames. There are three possibilities for the partial conversion of nitric acid to nitric oxide in passage through the inner cone; all the nitrogen in nitric acid does not follow the same reaction path, radicals formed in the inner cone react with nitric oxide, or a combination of these two. There is plenty of evidence for radical reactions in the inner cone, for the formation of CN and NH show that the nitrogen in some cases at least has broken its original bonds in the nitric acid. While it must be remembered that the concentrations of CN and NH are very small despite their prominence in the spectrum, small concentrations of radicals are often sufficient to maintain chains of considerable length. It has been pointed out by H. G. WOLFHARD and others[1, 2, 5] that nitric oxide can react with radicals like NH, probably via a low activation energy reaction as

$$NH\,(^3\Sigma^-) + NO\,(^2\Pi) = N_2\,(^1\Sigma) + OH\,(^2\Pi)$$

In the first combustion wave there are probably atomic species as well as molecular fragments, and these may also react with nitric oxide. G. B. KISTIAKOWSKY and G. G. VOLPI[15] have recently reported fast reactions between nitric oxide and N(^4S). It is unfortunate that the spectrum offers no more clues as to the role played by the radicals, particularly NH and CN, which are so prominent in the spectrum of these flames. Neither NH nor CN fits into any reaction mechanism that has been suggested. If considerable concentrations of atoms occur in the combustion zone, then NH might be formed by the inverse of dissociation, which is an exothermic reaction

$$N\,(^4S) + H\,(^2S) = NH\,(^3\Sigma^-)$$

and if N (^2D) is available, the upper level NH ($^3\Pi$) can be populated. Rather than speculate further as to the reactions leading to the production of N and H atoms, etc., the evidence presented indicates that radicals play an important role in the reduction of nitric acid to nitrogen, and in the reduction of nitric oxide.

The burning velocities given in *Figures 2* to *5* inclusive are for an oxidizer that is 91 mole per cent nitric acid, the remaining species being water, nitrogen dioxide and oxygen. It is possible that pure acid would have materially different burning velocities with the fuels investigated and that this might account for the difference between these results for acid and propane and those previously reported. It should be clear at any rate that the burning velocity depends upon the amount of dissociation of the acid vapour, for this determines the volume flow when the mass flow is known.

In comparison with oxygen, nitric acid, although a powerful oxidizer capable of producing high combustion temperatures, does not yield as high burning velocities with hydrocarbon fuels. With propane, the burning velocity with acid is only about one quarter that with oxygen. However, low burning velocities are characteristic of many nitrogen-containing oxidizers burning with hydrocarbons. Of interest is the fact that the pressure dependence of the burning velocity of nitric acid–*n*-heptane mixtures and of nitric acid–propane mixtures are in accord with some generalizations drawn by B. LEWIS[16].

What is most important is that over a fourfold pressure increase the nitric acid–propane flames did not change appearance at 400°K initial temperature. However, keeping the pressure constant and raising the initial temperature of the nitric acid–propane mixture yielded flames in which it was clear that the reactions downstream of the first combustion wave were speeding up. R. L. POTTER and D. H. WAYMAN[9], as a result of their work with nitric acid–*n*-heptane–nitrogen mixtures concluded that the detonation limits correspond to Chapman–Jouguet temperatures of 3000°K. From *Figure 6* it can be seen that the adiabatic flame temperature of nitric acid–propane mixtures, burning to equilibrium is 150° below 3000°K. Therefore if the final temperature is important in flames with nitrogen-containing oxidizers burning with hydrocarbons as regards completing the reduction of nitric oxide to molecular nitrogen, then preheating the combustible mixture should result in a change in the combustion characteristics. This indeed happened and, as predicted, the reactions in the hot gas downstream of the first combustion wave were fast enough to show a new wave in the absence of secondary air. From the results on detonations in nitric acid–hydrocarbon mixtures, it is clear that at some initial temperature and/or pressure the combustion must be nearly complete in a single reaction zone. From the experiments reported, it appears that the initial temperature is more important than the pressure in ensuring complete reaction in one wave in nitric acid–hydrocarbon mixtures.

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Some Recent Developments Concerning Free Radicals (A Review)

G. J. MINKOFF

The status of knowledge of several of the smaller radicals and atoms is considered with particular reference to those which take part in combustion processes.

WITHIN the last ten years, several techniques have been developed, or modified, to investigate the properties of free radicals. The achievements of each of these methods have been reviewed in some detail, in a journal[1] not readily available in the United Kingdom, and at two unreported conferences on the properties of free radicals (Quebec, 1956), and of trapped radicals (Washington, 1957). The aim of this review is therefore to consider the status of knowledge of several of the smaller radicals and atoms (particularly those which take part in combustion processes), both in the light of these, and other, sources of information. However, no attempt will be made to cover the subject of free radicals more widely, since this has recently been done by E. W. R. STEACIE[2]. The extensive photochemical investigations of free radical reactions and their kinetics will also not be considered here, since they would more properly form the subject of a separate review.

EXPERIMENTAL TECHNIQUES

Ultra-violet spectroscopy

Information is provided by the transition from one electronic level to a less energetic one (often, but not always, the ground state). As a result of the fine structure accompanying the main bands, and of the distribution of the intensity of individual lines, deductions can be made about the structure, shape and dimensions of the emitter (or absorber). The interpretations, however, are not clear-cut and, very often, the selection of one of several possible assignments is accompanied by much controversy. In general, monatomic and diatomic species can be analysed fairly readily, and recently, considerable progress has been made with triatomic species, in spite of considerable theoretical difficulties (see also A. G. GAYDON[3]).

Infra-red spectroscopy

Here, information is obtained as a result of changes in the vibrational quantum numbers of particular modes. Many of the observed bands are related, sometimes quite simply, to the vibration frequency of particular bonds within a molecule (e.g. $>C=O$, $>N-H$). Examination of rotational line structure and intensity distributions can again be helpful in determining structure. Additional information is provided by the number of bands

observed, this indicating the types of symmetry permitted. Considerable complications arise because the observed frequencies are always related to vibrations of the whole molecule, and not just to parts; and overlap of bands makes the symmetry deductions less certain. Many i.r. bands are affected by changes in temperature, since these alter the populations of the rotational levels, and hence the fine structure.

Paramagnetic resonance

Of the various forms of radio frequency spectroscopy which have recently been developed, paramagnetic resonance (PMR), or electron spin resonance (ESR), is particularly suitable for the study of free radicals[4]. It is concerned with transitions which may occur in a system containing an unpaired electron in the presence of a suitably directed magnetic field; two energy levels are then available, which correspond to two spin orientations. The transition can be caused by the application of a suitable frequency, usually of the order of thousands of megacycles per second. Studies of the energy absorbed yield information about the system in which the free electron is situated. Considerable difficulty, however, attends the interpretation of the observed spectra, and many workers have referred to the possible complications. Confusion may arise, for example, with transitions associated with trapped charges, such as *F* and *V* centres, so that additional evidence of the presence of radicals is usually welcomed. In crystals, interactions between the crystalline electric field and the orbital momentum of the unpaired electron can give rise to extra lines with anisotropic coupling constant (g) values.

Mass spectrometry

Much progress has been made in the mass spectrometry of free radicals since G. C. ELTENTON[5] and F. P. LOSSING with A. W. TICKNER[6] overcame the initial difficulties. Techniques for distinguishing the peaks of radicals from those due to fragments of the parent molecule are now well established. The ionization potentials of many radicals have been measured with the mass spectrometer, and valuable deductions have been made as to the energy required to form the radicals[7]. Several studies have been made of flames, active species being sucked through narrow probes into mass spectrometers.

The main difficulties are connected with losses of radicals by reactions on various surfaces, and in secondary processes. This hinders the quantitative estimations of unknown radicals, unless control methods are available. The development of time-of-flight mass spectrometers, in which spectra are scanned in microseconds, is opening up new fields of study.

The importance of heterogeneous and ionic reactions in conventional mass spectrometers used for free radical work has been stressed by S. N. FONER and R. L. HUDSON[8]. With water, for example, they found that even at 10^{-3} mm of mercury, ionic reactions were important because of the high probability for the reaction

$$H_2^+ + O_2 \longrightarrow HO_2^+ + H$$

Flash photolysis

One of the most fruitful of recent techniques has been the method due to R. W. G. NORRISH and G. PORTER[9] of creating large concentrations of radicals by liberating very large amounts of light of suitable wavelengths in a very short time. The absorption spectra of subsequent events are then recorded by viewing a number of successive, high intensity and short duration flashes through the reacting gases. Two types of applications have been reported: first the study of radical reactions[10], and secondly the spectroscopy of individual radicals (G. HERZBERG and D. A. RAMSAY[11]). The use of photomultipliers coupled with oscilloscope presentation made possible continuous studies of explosion processes (R. W. G. NORRISH *et al.*[12]; H. P. BROIDA *et al.*[13]). Many aspects of kinetic spectroscopy have been investigated by R. W. G. NORRISH and B. A. THRUSH[14]. Difficulties are associated with uneven heating, and the development of localized high energy regions[15], and also with the separation of chemiluminescence from thermal radiation; the former is increased by a reduction in pressure, while the opposite holds for thermal radiation (G. J. MINKOFF *et al.*[16]).

Shock tube methods

The use of shock tubes for examining combustion processes has become widespread in the last few years, and many applications have been reported (R. W. PERRY and A. KANTROWITZ[17], E. F. GREENE[18], A. R. FAIRBAIRN and A. G. GAYDON[19, 20]). An attractive feature is that very high temperatures (up to 10 000 to 18 000 °K) can be induced in gases for a very short time, since a cooling wave follows closely. It is thus possible to study the time required for the equipartition of energy between the translational, electronic, vibrational and rotational degrees of freedom. Pyrolysis can also be examined, since the presence of an oxidizer is not necessary for high temperatures to be obtained. Another useful feature is that the spectra obtained are much closer to thermal equilibrium than those produced in electrical discharges.

Low temperature trapping of radicals

G. N. LEWIS and D. LIPKIN[21] observed in 1942 that when certain aromatic compounds were photolysed in glasses at low temperatures, unstable species were formed which did not immediately disappear on standing. F. O. RICE and M. FREAMO[22] showed later (1951) that coloured, active species could be trapped on a cold finger from the products of high temperature pyrolysis. The use of a matrix of more or less non-reactive molecules for stabilizing atoms and radicals was investigated by I. NORMAN and G. PORTER[23], E. WHITTLE *et al.*[24], and others. A great deal of work has now been carried out (for reviews, see H. P. BROIDA[25], G. J. MINKOFF[26]), both with radicals chilled on to a cold surface, and with radicals formed within the matrix at a low temperature.

Clearly, many other techniques could have been referred to, such as the chemical combination of radicals with metals or other substances as first used by Paneth. However, the aim of this brief description has been to include those with the widest applications, and to draw attention to any

important deficiencies. In this connection, little has been said about the quantitative aspects. Clearly, estimates of relative amounts can always be carried out, by calibration, if the concentrations can be controlled at will. An elegant example is the method due to G. PORTER, B. A. THRUSH and R. W. G. NORRISH[27] of changing the length of the absorbing tube by factors of one half in successive experiments. Often, however, more complicated systems are investigated, and, without perfect resolving power and knowledge of all the transition probabilities and populations, only qualitative deductions can be made from optical and radio spectroscopy.

THE SIMPLER RADICALS

Let us now consider the situation with regard to the simpler radicals, in the light of results obtained mainly by the techniques described above (i.e. not by conventional kinetic and photochemical methods).

Radicals composed only of H *and* O

H *atoms*—Visual and u.v. efforts to study trapped H atoms at 4°K have not so far been successful, although the deposit does not have the same appearance as hydrogen not subjected to the discharge, but frozen in the same way[25]. The PMR spectra of free H atoms have been reported by R. BERINGER and M. A. HEALD[28]. C. K. JEN *et al.*[29] produced H and D atoms from electric discharges, and deposited them on a sapphire rod at 4°K. After deposition, this rod (still connected to the liquid helium reservoir), was inserted into a rectangular microwave cavity. This cavity, which was kept at 77°K, was operated in the 'TE012 mode'. For hydrogen, two lines of almost equal intensity were observed. One was 234·1 oersteds above the field for free electron resonance, the other 274·6 below. Deuterium had three lines, separated by 76·7 and 78·7 oersteds from the centre line, which was 2·1 oersteds below the free electron value. These are consistent with the known hyperfine structures of free H and D. From the deduced coupling constants and g_J values, it appears that the trapped atoms are not absolutely free. Other strong, sharp lines were observed, as triplet and quartet groups, which may be associated with excited molecules.

The presence of atomic hydrogen has been also rigorously established, by R. LIVINGSTON, H. ZELDES and E. H. TAYLOR[30, 31], who irradiated a number of acids at 77°K. The relevant lines consisted of a pair, which appeared in all the acids, with constant separation and relative intensities. Weak satellites indicate weak magnetic interaction with neighbouring protons; their intensity relative to the main line gives a measure of the distance from the H atom to the nearest protons.

Possible sources of misinterpretation are emphasized.

The products of γ-irradiation of ice have also been investigated by B. SMALLER, M. S. MATHESON and E. L. YASAITIS[32] and by M. S. MATHESON and B. SMALLER[33]. At 77°K, a doublet was obtained from H_2O, 30 gauss apart, with line widths of 6 gauss, while D_2O gave a triplet. The presence of a free spin near to an H or D nucleus was indicated. The splitting effects were less than in the gas phase, presumably because of the effect of the crystal field on the electronic state of the H or D atoms.

It is believed that the spectra were due to H and OH radicals. The PMR spectra of H atoms have been discussed in some detail because there is a strong probability that the interpretations are correct. This is less certain with more complicated radicals.

The role of absorbed H atoms in quenching low pressure flames, and in destroying hydrogen peroxide on very cold walls, has been discussed by A. J. EVERETT and G. J. MINKOFF[34].

O atoms—Attempts to obtain the PMR spectra of trapped O atoms have not so far been successful[35]. The presence of oxygen atoms in the products of a microwave discharge through oxygen has been shown, quite conclusively, by the formation of ozone, either on trapping at low temperatures or on warming the frozen gases[36]. In the presence of argon, R. RUHERWEIN *et al.* have found that ozone can be the sole product, indicating that at least one third of the original oxygen must have been dissociated. The presence of oxygen atoms in the gas has also been confirmed by mass spectrometer studies (J. HERON and H. I. SCHIFF[37]), though the indicated concentration is lower. The problem of deciding the relative importance of ozone formation at the trapping stage, and during the warm-up, has not yet been resolved. Although both are likely to be important, conflict exists at present because i.r. studies show that during warm-up[38] the ozone concentration does not appear to change.

OH—In the chilled products of electric discharges through water vapour (at 77°K), R. LIVINGSTON *et al.*[39] observed a main peak at $g = 2{\cdot}0085$, with a shoulder at 2·027. It is just possible, they suggest, that these bands could very tentatively be assigned to OH and HO_2. The same bands were also obtained under other conditions. The great complexity of the interpretation has been emphasized by these workers.

Trapped OH radicals have been shown to be present by the u.v. spectrum observed by G. W. ROBINSON *et al.*[10], from the condensed products of a discharge through hydrazine with a trace of water, frozen in an argon matrix at 4°K. Other (i.r.) attempts to detect trapped OH radicals have so far been unsuccessful.

In flames (A. G. GAYDON[3], H. G. WOLFHARD and D. S. BURGESS[11]) the study of rotational temperatures of OH continues. H. P. BROIDA and H. J. KOSTOWSKI[12] used a single and double path method to show that in the burned gases of highly diluted acetylene–oxygen flames at atmospheric pressure, self-absorption does not affect the rotational temperature measurements. The controversy begun by S. S. PENNER[13] is thus finally settled. The lifetimes of excited OH in flames has been examined by H. P. BROIDA and T. CARRINGTON[44, 45], using a fluorescence method. They found that quenching occurs at every collision. The mechanism for the degradation of the rotational excitation[3] is not at present understood. H. J. KOSTOWSKI and H. P. BROIDA[46] have also used the OH absorption to measure temperatures without requiring very high resolution; this is accomplished by using as source OH emission at a lower temperature than the OH in the flame, the source line width thus being much narrower. The mechanisms for the production of excited OH have been reviewed by Gaydon[3]. The effect of lead ethyl on the OH emission and absorption in acetylene–oxygen–

amyl nitrate mixtures has recently been examined by K. H. L. ERHARD and R. W. G. NORRISH[47], using the flash technique.

Before 1954, the relative amount of OH in discharges through water vapour was often estimated by measuring the concentration of H_2O_2 found when the gases were passed through a trap at 77°K, or by detecting the heat liberated by recombination on thermocouples coated with potassium chloride. G. H. TOWNES *et al.*[48], who were attempting to record the microwave spectrum of OH, discovered that the OH concentration, when measured by means of this spectrum (or of the u.v. spectrum, with sufficient resolution), did not affect the peroxide yield, and varied the heat liberated on the couple. These conclusions agree with those of D. R. WARREN[49] and of R. R. BALDWIN and R. F. SIMMONS[50], based partly on work with H_2–O_2 explosion limits, where potassium chloride appears to destroy HO_2 much more efficiently than OH. The problem is discussed further in the next section in connection with the formation of hydrogen peroxide.

HO_2—Apart from the possible PMR spectrum, the presence of HO_2 has not yet been directly established in the solid or trapped phase, and it has only been identified in the gas phase by mass spectrometry. The pioneer work of P. A. GIGUÈRE and E. A. SECCO[51], and P. A. GIGUÈRE[52], in which they examined the i.r. spectrum of the chilled products of a discharge through water, was complicated by the presence of traces of nitrogen oxide[53]. Although the band originally assigned to HO_2 (1 305 cm^{-1}) agreed well both with that predicted by transition state theory (G. J. MINKOFF[54]) and by third body efficiencies (A. D. WALSH[55]) the absorbing molecule was eventually found to be N_2O_3. Another type of evidence proposed for HO_2 was the evolution of oxygen when the products warmed up to −120°C (R. A. JONES and C. A. WINKLER[56]). However, recent low temperature studies by J. W. EDWARDS and J. S. HASHMAN[57] have shown that the oxygen is originally trapped into molecular complexes with several molecules of hydrogen peroxide, depending on the precise chilling conditions.

Mass spectrometric techniques have proved the existence of HO_2 (G. C. ELTENTON[5], A. J. B. ROBERTSON[58], and S. N. FONER and R. L. HUDSON[59]), and have yielded a value of 47 kcal for $D_{(H-O_2)}$. Although HO_2 has been found by this technique in the decomposition products of hydrogen peroxide, and in some combustion systems, such as hydrogen–oxygen, controversy has arisen because Foner and Hudson, at low pressures, found only H_2O and OH. It is not clear whether these, or HO_2, are the primary products. Robertson has suggested that the H_2O and OH could be formed in secondary reactions such as:

$$H + HO_2 \longrightarrow 2\,OH$$
$$OH + HO_2 \longrightarrow H_2O + O_2$$
$$H + H_2O_2 \longrightarrow OH + H_2O$$

More information is clearly required. The HO_2 radical has also been detected by K. U. INGOLD and W. A. BRYCE[60] in the hydrogen–oxygen reaction at 1 000°C, with a short contact time.

Although our understanding of the reactions of HO_2 is now increasing considerably as a result of kinetic and explosion limit studies, a major

difficulty still attends the mechanism of formation of hydrogen peroxide on cold surfaces. One aspect of this involves the effect of trapping temperature on the yields of peroxide from discharges through water vapour and from the hydrogen–oxygen system, similar curves being obtained for the two systems. Jones and Winkler[56], who made this observation, therefore proposed a set of reactions involving a common intermediate precursor to peroxide formation. However, it has also been pointed out (G. J. Minkoff[61]) that at 190°K, the hydrogen–oxygen system produces water, while the water vapour system gives molecular hydrogen and oxygen. It is thus necessary to reconcile a difference as well as a similarity. The other difficulty is to account, within the same framework, for the absence of peroxide formation at 190°K from the discharge systems, and the considerable amounts of peroxide chilled out at 190°K from explosion products (Everett and Minkoff[34]). The reactions deduced to be operative in the latter should contribute whatever the source of the radicals.

The lifetime of HO_2^* formed in bimolecular collisions, not stabilized by further collisions, has been deduced to be of the order of 10^{-8} second by R. Burgess and J. C. Robb[62]. These workers were examining the photochemical, mercury sensitized, hydrogen–oxygen reaction by the thermal method developed by A. B. Callear and J. C. Robb[63].

Radicals containing carbon

Considerably less work has been carried out with small carbon-containing radicals because of the greater difficulty of preparing radicals of known structure, and because of the considerable fouling of the apparatus by the carbonaceous deposits and tars sometimes formed in the discharge. Most of our knowledge of radicals such as CH and C_2 and HCO has come from spectroscopic studies of flames, and of flash photolysis and shock wave products. The OH, CH and C_2 radicals are often interdependent, and they will therefore be considered together, somewhat later in the section.

C—Very hot flames of carbon-rich fuels can emit a line at 2478Å which is due to the $3s\,^1P^0 \longrightarrow 2p^2\,^1S$ transition of atomic carbon[3]. Recently, however, it has been observed[64] at lower temperatures. A. G. Gaydon and A. R. Fairbairn, who were studying the CO afterglow, and its reactions with acetylene, found the line in the products of the condensed discharge, as well as some lines due to ionized carbon.

C_2—The well known C_2 Swan bands were also observed by Gaydon and Fairbairn[64], from the uncondensed discharge, but the afterglow consisted of the high pressure bands of this system, in which $v' = 6$. G. Herzberg[65] has suggested that the formation of vibrationally excited C_2 radicals follows from the recombination of free carbon atoms. When acetylene was introduced, considerable amounts of carbon were formed, possibly by reactions such as

$$C_2 + C_2H_2 \longrightarrow C_4 + H_2$$

The mechanism of the formation of C_2 in flames was investigated by R. Ferguson[66], who burned acetylene 40 per cent enriched with ^{13}C. The relative abundances of ^{12}C and ^{13}C in the C_2 emission were accurately measured and compared with the mathematically analysed ratios predicted

for two possible modes of formation of excited C_2. The first involves stripping of the H atoms from an acetylene molecule, while the other is concerned with a chain of reactions in which the —C≡C— band of acetylene is broken. The latter was indicated to be the more important.

C_3—This is known mainly through the 'comet head band' at 4050Å which was for some time suspected of being emitted by CH_2. A. E. DOUGLAS[67], however, showed that C_3 was the emitter by using carbon isotopes to affect the spectrum. In combustion processes, C_3 was first observed in absorption during flash sensitized explosions of hydrocarbons with oxygen[27], and in emission, from rich acetylene–oxygen flames by N. H. KIESS and H. P. BROIDA[68]. The high resolution spectrum has been analysed by N. H. KIESS and H. P. BROIDA[69] and by K. CLUSIUS and A. E. DOUGLAS[70].

A rather unusual method of formation has been revealed by the flash photolysis of diacetylene (J. H. CALLOMON and D. A. RAMSAY[71]). At a pressure of *ca.* 0·5 mm of mercury, absorption systems of C_2 (Swan, Phillips and Deslandres-d'Azambuja) were recorded after 20 microseconds, and also the CH band at 3143Å and the 4050Å C_3 band. The rotational temperatures were of the order of 3000 to 5000°K. When a 100-fold excess of helium was added to the diacetylene, only the C_3 bands remained (with unchanged intensity). The rotational structure now indicated approximately room temperature. The absence of C_2 is quite surprising, since the middle C—C band is weak. Presumably some predissociation to $C_3H + CH$ may occur.

CH—Apart from its occurrence as a fragment in mass spectroscopy, the properties of this radical are based mainly on those obtained from its u.v. spectrum in flames[3]. Its use for measuring flame temperatures has been discussed by A. G. GAYDON and H. WOLFHARD[72] and by H. P. BROIDA[73]. Recently, detailed analyses have been made of the (0,1) and (1,2) bands of the $^2\Delta \longrightarrow {}^2\Pi$ system[74].

The results obtained by kinetic spectroscopy have been reviewed very extensively[14, 75], and the original literature may be consulted for details of the time dependence of OH, C_2 and CH radicals in sensitized explosion phenomena. The mechanism of formation of the excited radicals, in the various modes, has also been discussed by Gaydon[3]. An important development involving the three radicals concerns their distribution in a low pressure oxyacetylene flame (H. P. BROIDA and D. F. HEATH[76]). The use of photoelectric measurements of intensities permitted the determination of trends within the luminous zones with increased resolution. A new region was found at the base of the luminous zone, one tenth of the thickness of the latter, with increased C_2 and CH emission relative to OH, and higher 'vibrational temperatures' than are observed elsewhere in the flame.

Shock wave studies of these, and other, radicals have been made both in absorption (C. F. ATEN and E. F. GREENE[77], and C. E. CAMPBELL and I. JOHNSON[78]), and in emission (Greene[18], Gaydon and Fairbairn[19], and Clouston and Gaydon[20]). Time resolution studies by the latter support the reaction usually proposed for the formation of CH

$$C_2 + OH \longrightarrow CH + CO$$

CH_2—This spectrum is still unknown.

CH_3—The main development here has been the identification by G. HERZBERG and J. SHOOSMITH[79] of the u.v. absorption spectrum. They decided that the failure to find such a spectrum might be attributed to the planarity of CH_3 (predicted by A. D. WALSH[80]), which would cause the electronic transition to be forbidden. The vacuum u.v. was therefore searched for the strongly allowed transitions of the Rydberg type. The radicals were produced by flash photolysis of mercury dimethyl at a pressure of 0·04 mm of mercury, with a 3 m vacuum grating spectrograph. Four narrow groups of diffuse absorption bands were found in the region 1 510 to 1 300Å. Similar bands, slightly shifted, were found from the photolysis of $Hg(CD_3)_2$. At slightly longer wavelengths, the two compounds gave rise to a band at 2 160Å from the former, and 2 140Å from the latter. These are less interfered with by the parent compound than are the shorter wavelength bands. Similar bands were then obtained by the photolysis of other methyl derivatives.

The principal bands gave rise to Rydberg series, in which the ionization potentials are indicated to be *ca.* 9·84 in excellent agreement with the electron impact values of 9·90 ± 0·1 eV. Confirmation has also been obtained by the photolysis of partly deuterated acetones, and the detection of new bands due to CHD_2 and CD_2H. With one exception, all the bands were diffuse, as a result of predissociation. The CD_3 band at 2 140Å, however, which has some structure, shows a slight intensity alternation which would be in accord with a planar radical, with a small amount of inversion. The methyl radical has also been observed in low temperature trapping experiments (I. L. MADOR[81]). It was obtained by photolysing methyl iodide at 4·2° K. On warming, violent disintegration took place at 30 to 40° K, with the formation of iodine. Experiments were also carried out with x-radiation of lead tetramethyl at 4·2° K, a violent change again being observed at 40° K. The presence of PMR bands due to CH_3 groups in solids irradiated at 77° K has been reported by W. GORDY and C. G. MCCORMICK[82].

HCO—The formyl radical has been of interest recently partly in connection with discussions of $D_{(H-CO)}$, and partly in connection with preignition glows, the spectra of which have been examined by Gaydon and Moore. Extensive analyses of the spectra of HCO and DCO have also been carried out.

The dissociation energy has been the subject of controversy for some time (Steacie[2]), estimates varying originally from 0 to 26 kcal. More recently, two possible values have been proposed: 14 kcal, by J. G. CALVERT and E. W. R. STEACIE[83] and by E. C. A. HORNER *et al.*[84], and 27 kcal, proposed by E. GORIN[85] and by L. SCHOEN[86]. Part of the uncertainty lies in the primary act

$$H_2CO + h\nu \longrightarrow H + HCO \quad I$$
$$\searrow H_2 + CO \quad II$$

Reaction II is known to be unimportant above 300° C, but the extent to which it participates at lower temperatures (100 to 150° C) is unknown.

R. KLEIN and L. SCHOEN[87] therefore photolysed H_2CO and D_2CO, alone and mixed. They estimated the deviation of the apparent equilibrium constant of the H—D equilibrium, and deduced the relative importance of processes I and II. At 300°C, the split to H and HCO is favoured, particularly at 3 650Å, long chains being obtained. At the lower temperatures chain lengths were greatly reduced, and the intramolecular split is favoured.

Klein and Schoen also showed that the upper wavelength limit for the primary process is 3 650Å, corresponding to 78 kcal for $D_{(H-HCO)}$. The lower limit for $D_{(H-CO)}$ is then 27 kcal. Calvert and Steacie's value thus appears to have been affected by the presence of chain reactions.

These values agree well with those deduced by R. I. REED[88] by electron impact methods, namely 74·4 kcal and 30·4 kcal respectively. They were carefully shown to be free of interfering factors such as kinetic energy in the fragments.

The emission of the formyl radical is normally observed best with weak mixtures[3], and is strengthened by chilling the flame. It is therefore interesting to note that HCO emission has been detected in rich mixtures, in the region of pre-ignition glows. A. G. GAYDON and N. P. W. MOORE[89] suggest that under these conditions, chain branching is not sufficient to give rise to full explosion, so that chain-terminating reactions, associated with the HCO, may be of special importance.

Finally, let us consider the analysis of the HCO absorption system (4 500 to 7 500Å). This was first observed[90] in the flash photolysis of some aldehydes, and consisted of two bands with heads at 6 138 and 5 624Å. They had a simple structure, and indicated a transition from a bent lower state to a linear upper state. More bands of both HCO and DCO have now been observed[91]. Two diffuse bands have also been reported, and it is possible from these to suggest an upper limit of 37·7 kcal for $D_{(H-CO)}$.

A complete rotational analysis of the sharp bands has permitted deductions regarding the dimensions. Assuming reasonable values for the C—H bond lengths, the angles are found to be $119\frac{1}{2}°$ in the lower state, and 180° in the upper, while the C—O lengths change little. In agreement with the Franck–Condon principle, the spectrum therefore consists of a long progression of the bending vibration in the upper state.

Radicals containing nitrogen

N—Nitrogen atoms, trapped at 4°K from a microwave discharge through nitrogen, have received much attention, partly as a result of the green glow and brilliant blue and white flashes which accompany the deposition (L. VEGARD[92], J. C. MCLENNAN and I. SHRUM[93], H. P. BROIDA and J. R. PELLAM[94]). Exhaustive studies of the various bands emitted have been made (see Minkoff[26] for detailed references) and the interpretation has thrown much light on the forces in the lattice. The main features of the spectrum of the green glow are the five α lines (blue-green) at 5 230Å, and the (yellow-green) β bands at 5 575Å. The former are emitted by N atoms in the ^2D state returning to the ground state (^4S), while the β bands are emitted by O atoms returning from the ^1S to the ^1D state (these are

present as an impurity). Blue bands are emitted during recombination reaction, the corresponding 'A' system being identified rigorously (C. M. HERZFELD and H. P. BROIDA[95]) with the transition from the $^5\Sigma$ to the $^3\Sigma$ state of molecular nitrogen. In the presence of excess argon, the blue Vegard–Kaplan bands are also observed[96], corresponding to the $A\ ^3\Sigma—X\ ^1\Sigma$ transition of molecular nitrogen. Above 35·5°K, a phase change occurs in the nitrogen lattice, and the remaining unstable species are no longer stabilized. The concentration of atoms is still the subject of controversy, but both calorimetric[97] and chemical methods[36] indicate the presence of a few atoms per cent.

The trapped nitrogen atoms have also been examined by PMR, both by S. N. FONER *et al.*[98] and by T. COLE *et al.*[99]. The former used a number of solid matrices to trap the nitrogen in order to decide why the spacing in the observed triplet was different from that in the gas phase. The hyperfine coupling was found to increase on passing from hydrogen to N_2 and CH_4 matrices, in the order of increased binding energies. The g factor, however, remained unchanged. For N, their value was larger than that of Cole *et al.* These results show that the N atom is considerably affected by the presence of the matrix molecules. Similar conclusions were reached by H. P. BROIDA and M. PEYRON[96], and C. M. HERZFELD[100], from further experimental and theoretical studies of the u.v. spectrum.

Most other studies of N atoms, at higher temperatures, have been associated with the 'active nitrogen' problem. The considerable number of recent researches have been reviewed by K. R. JENNINGS and J. W. LINNETT[101]. We may mention here some of the chief features. They include J. N. BENSON'S[102] demonstration that the electron concentration is less than 10^{-6} of that of the active species, and a number of estimates of the free atom concentration which vary from 3 to 30 per cent. The suggestion that the weaker bands observed in the afterglow are not members of the First Positive System, but of a separate series due to transitions between unknown levels of nitrogen, has opened up a new approach (G. KISTIAKOWSKI and WARNECK[103]).

A detailed discussion then shows that most of the observed phenomena can be explained on the basis of the scheme:

$$\left.\begin{array}{l} \nearrow a\ ^1\Pi_g \longrightarrow X\ ^1\Sigma_g^+ \text{(Lyman–Byrge–Hopfield)} \\ \text{N}(^2S) + \text{N}(^4S) + \text{M} \longrightarrow \text{N}_2(^5\Sigma_g^+) \longrightarrow B\ ^3\Pi_g \longrightarrow A\ ^3\Sigma_u^+ \text{ (First Positive)} \\ \searrow Y \text{ state} \longrightarrow Z \text{ state (Proposed New Bands)} \end{array}\right.$$

The observation of the $^5\Sigma_g^+$ state in the trapped N atom studies gives strong support.

This review should also be consulted for references to recent studies of the interaction of active nitrogen with some nitrogen oxides.

N_3—Although D. E. MILLIGAN *et al.*[104] suggested that some of their i.r. bands could be explained by the presence of trapped N_3, K. B. HARVEY[105] was unable to reproduce these bands when very pure nitrogen was used. Bands attributed to N_3 have been reported by B. A. THRUSH[106], who observed an absorption system around 2700Å during the flash photolysis of hydrazoic acid.

NH—Apart from the many observations of NH bands[3] in flames or flas sensitized explosions[14], the NH radical is of considerable interest becau it is probably the first radical to be intentionally frozen out. This w done by Rice and Freamo[22], in 1951, in connection with the elucidation the mechanism of decomposition of hydrazoic acid. When the produc were passed over a finger cooled to 77°K, a blue solid was deposited whic later decomposed explosively on warming. Numerous researches ha since been carried out to determine whether the NH radical was in fac isolated or not. Here, as in so many instances, mass spectrometry gave negative result. However, the majority of the recent observations suppo Rice's interpretation, although it is difficult to decide whether the radica is present in trace amounts only, or in larger proportions. The definit evidence of traces, at least, of NH comes from u.v. spectra of the glow of trapped, discharged[26] nitrogen of only moderate purity—deductions about the crystal forces again being possible.

Infra-red examination of the products of decomposition of HN_3 has yielded strong evidence. The extensive results of D. A. Dows *et al.*[107] are in accord with the freezing out, at 90°K, of HN_3, NH_4N_3, $(NH)_x$, and the blue, paramagnetic NH radical. Warming slightly permits dimerization of the latter, with the formation of N_2H_2 (dimide), while HN_3 and any NH_3 combine. At higher temperatures, the polymer rearranges to NH_4N_3, and the dimerization of N_2H_2 gives the same product. The $(NH)_x$ polymer probably has unpaired electrons and contributes to the blue colour and to the paramagnetism.

NH_2—The u.v. spectrum of trapped NH_2 has been reported by G. W. Robinson *et al.*[108] in the chilled products of a discharge through hydrazine vapour mixed with excess argon. Owing to the sharpness of the spectrum a 2 m grating was used, and 12 lines were observed. Their positions corresponded closely to those in the gas phase (see below), except for a 25 cm^{-1} shift to the blue. The alternate bands are missing, because the initial state (15 cm^{-1}) is insufficiently populated at the very low temperature.

The high temperature bands were first observed in absorption by G. Herzberg and D. A. Ramsay[109], as a product of the flash photolysis of ammonia and of hydrazine. Isotope shifts when ^{15}N and D were used supported the assignment. With shorter flash times and longer absorbing paths, a preliminary rotational and vibrational analysis was made (D. A. Ramsay[110]). The 3 : 1 intensity alternation in the branches provide unequivocal evidence of a twofold axis of symmetry. The upper state wa shown to be linear, and the lower state to be bent, with an H—N—H angl of 103°. The N—H bond length in the ground state of NH_2 was inter mediate between the values in the diatomic NH radical and in ammonia The Renner interaction has been described by D. A. Ramsay and K. Dressler[111]. Chemical attempts to trap NH_2 radicals were not entirel successful (F. O. Rice and F. I. Scherber[112]), as the products were too complicated.

HNO—The u.v. spectrum of trapped HNO was obtained during the freezing of products of a discharge through hydrazine, with a little moisture in the presence of excess argon. The vibrational frequencies, 1422 and

98[illegible] cm^{-1}, were identical with the gas phase values. These were obtained by F. W. DALBY[113] during the flash photolysis of ammonia mixed with nitric oxide, and a small shift was observed when ND_3 was used instead. These bands have also been reported in the photolysis of deuterated acetaldehyde, because of traces of nitrogen impurities.

Clearly, many radicals have not been included, for reasons of space, but references will be found in the reviews by D. A. RAMSAY[111], F. P. LOSSING[6], and G. PORTER[115], as well as those already mentioned. The developments in the study of the reactions of excited states have also been referred to by Porter, and they have formed the subject of a recent monograph[116] and of a conference held by the Canadian Institute of Chemistry[117]. Their role in reaction mechanisms is becoming considerably clearer.

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Recent Developments and Notes

THEORETICAL FLAME TEMPERATURES

J. W. MYERS, S. A. GOLDBERG and R. W. SMITH, Jr, of the U.S. Bureau of Mines, Pittsburgh, have recently published a paper on the calculation of theoretical flame temperatures in furnaces [*Trans. Amer. Soc. mech. Engrs* 80 (1958) 202]. The work was sponsored by the American Society of Mechanical Engineers Special Research Committee on Furnace Performance Factors. During the past twelve years an investigation at intermittent intervals has been carried out on the performance of large steam generators. The present work has been necessitated in order to determine whether, by analysing the accumulated data, a generalized correlation of furnace heat-absorption efficiency can be obtained in terms of the operating variables of a particular furnace.

The thermodynamic data are presented in graphical form to determine adiabatic flame temperatures for combustion processes at atmospheric pressure and the data are applicable for coal, coke, and liquid and gaseous hydrocarbon fuels when burned with air at values of excess air ranging from 0 to 100 per cent. A technique for using electronic computing machines to calculate the equilibrium composition and enthalpy of gaseous products of combustion is discussed.

The data are presented in a generalized form so that the heat of dissociation and the total enthalpy can be determined for any gas composition within the range considered and for any temperature between 1 320 and 2 200°C. Conversely, the adiabatic flame temperature may be determined if it lies between these limits and if the enthalpy of the system is known. Plots of the heat of dissociation of flue gases enable flame temperature to be determined with an accuracy of ±10°C by means of additional calculations and auxiliary plotting. Only the four gas components are considered, carbon dioxide, water vapour, oxygen and nitrogen, and the error introduced by including sulphur dioxide with carbon dioxide when burning a high-sulphur fuel is less than 5°C at extreme conditions of temperature and excess air.

The work is similar to that of P. ROSIN and R. FEHLING in their *T* diagram of combustion (VDI-Verlag: Berlin, 1929). Their work was more comprehensive than the present investigation, but the approach was not so rigorous, and the work less detailed and less accurate, owing to the simplified assumptions that were made. Further, more accurate thermodynamic data are now available than at the time of Rosin and Fehling's work.

NEW DESIGN FOR BOILER FURNACE

A new design for a boiler furnace which it is claimed considerably increases the mixing efficiency of the combustion gases has been described by F. VOLLHARDT [*Brennst.-Wärmekr.* 9 (1957) 371]. The new feature consists

in fitting above the grate of a travelling-grate stoker a water-cooled triangular roof lined on the outside or inside with refractories and to draw the incompletely burnt gases to the front where they are mixed with secondary air before entering the main furnace. It is said that by this means stratification of the combustion gases is largely prevented. Refractories on the inside act like an arch and improve the ignition of fuels of high moisture content or of high ignition temperature. In one installation the carbon dioxide content of the flue gases was increased from 12 to 14·4 per cent, the excess air reduced to 1·28 and the thermal efficiency increased by 1·5 per cent.

ENGINE SURFACE IGNITION AND PHOSPHORUS COMPOUNDS

Whilst phosphorus compounds have been used for many years as additives to lubricating oils, it was only about five years ago that such compounds began to be used as commercial additives for motor fuels to control spark-plug fouling and pre-ignition. To what extent different phosphorus additives are effective in controlling surface ignition in engines and the effect of various engine parameters on the value of such compounds, have been studied by J. B. HINKAMP and J. A. WARREN, of Ethyl Corpn, Detroit [*Industr. Engng Chem.* (*Industr.*) 50 (1958) 251].

The phosphorus concentration of interest as a gasoline additive is from 0·2 to 0·5 of the quantity theoretically necessary to convert the tetraethyl lead present to orthophosphate. In fuel containing 3·0 ml of tetraethyl lead per gallon, this is equivalent to 0·06 to 0·15 g of phosphorus per gallon. Trialkyl phosphates, alkyl aryl phosphates, triaryl phosphates, 2-chloroalkyl phosphates, phosphonates, phosphites and some inorganic phosphorus compounds were used in the investigation. Some of these compounds markedly reduce the incidence of surface-ignited flame fronts. The effectiveness of the additives progressively increases as operation of the engine is continued for some hours until an equilibrium condition is reached. Hence phosphorus appears not to exert its effect by a vapour phase reaction, but rather by altering the composition of the deposit causing surface ignition. The temperature required to initiate glowing oxidation of the organic deposit constituents is thus raised by the complex lead–phosphorus compounds formed in the engine deposits. It was experimentally shown in this work that not only does phosphorus reduce the frequency of surface ignition but it also reduces the severity of those surface ignitions that are not altogether eliminated.

AEROTHERMODYNAMICS

Professor W. R. HAWTHORNE, F.R.S., Hopkinson and I.C.I. Professor of Applied Thermodynamics in the University of Cambridge, delivered a discourse in March at the Royal Institution on 'Aerothermodynamics'. He said that aerothermodynamics deals with the behaviour of flowing gases in which appreciable changes of temperature or density occur. Much of our knowledge of aerothermodynamics has been acquired as a result of the study and development of new methods of propelling aircraft.

He gave examples of aerothermodynamic phenomena which occur in the turbojet engine invented by Sir FRANK WHITTLE, and explained that because gas expands as it drops in pressure a convergent–divergent shape is required for a duct or nozzle which is intended to accelerate a gas. The maximum flow through such a nozzle is reached when the gas velocity at the minimum cross section reaches the velocity of sound. In the flow along a long pipe there is a pressure drop as a result of friction. If heat is added to the flow the expansion of the gas also causes an increase of velocity and a pressure drop. Heat addition or friction may therefore result in the velocity reaching the velocity of sound. When the velocity does reach that of sound the flow reaches its maximum. These effects limit the amount of air that can be passed through a jet engine thereby limiting the power that can be obtained with a given size and weight.

Although combustion in flames is a chemical phenomenon it has been found that the rate of combustion is limited by the rate of aerodynamic mixing and turbulence. Close control over the mixing and turbulence in the combustion chambers of jet engines is necessary in order to keep them compact. Another problem in combustion is that of keeping the flame alight in the high speed stream of air entering the combustion chamber. This is often done by stabilizing the flame in the wake of a baffle where the hot burnt gas can re-circulate to light the incoming cold mixture of air and fuel.

Although the turbojet engine has a compressor and turbine it is possible to propel an aircraft by combustion only. The ramjet, for instance, is a tube into which air flows at one end. Fuel is injected to mix and burn with the air in the tube and the products of combustion are discharged downstream in a high speed jet which propels the aircraft. This device has been called an *aerothermodynamic duct*.

Another aerothermodynamic device is the rocket which has a combustion chamber into which liquids such as oxygen and paraffin are pumped. They burn intensely in the combustion chamber and pass out through a convergent–divergent nozzle into the atmosphere or, perhaps, into space.

SECOND GENEVA ATOM CONFERENCE

In July last year it was announced that the British Government had accepted an invitation from the Secretary-General of the United Nations to participate in a second International Conference on the Peaceful Uses of Atomic Energy, from 1 to 13 September 1958.

The provisional agenda agreed by the seven-nation Advisory Committee covers all aspects of the peaceful applications of atomic energy. The President of the Conference is to be Professor F. PERRIN of the Commissariat a l'Energie Atomique de France and the Secretary-General, Dr S. EKLUND of Sweden.

Arrangements for the United Kingdom's participation are being organized by an Executive Committee of which the Chairman is Sir JOHN COCKCROFT and the Secretary, B. W. MOTT. The Secretariat is operating from the Atomic Energy Research Establishment, Harwell.

The Papers Committee has considered the suitability of a large number of suggested papers and has selected about 200 for submission to the United Nations. This represents about 10 per cent of the total number expected from all participating countries. Two atomic energy exhibitions will be held in Geneva during the Conference.

The U.K. delegation is expected to consist of five delegates, about 250 advisers and about 250 observers, the advisers being drawn primarily from among the authors of papers. The leader of the U.K. delegation will be Sir JOHN COCKCROFT, Member for Scientific Research of the United Kingdom Atomic Energy Authority. The other four delegates are expected to be a second representative of the Authority and representatives of the Royal Society, British industry, and the Medical Research Council.

ANALYSIS OF IONS IN FLAMES

A communication has been made by P. F. KNEWSTUBB and T. M. SUGDEN, of the Department of Physical Chemistry, University of Cambridge, of a method that they have devised for the direct mass-spectrometric analysis of ions drawn from a flame [*Nature, Lond.* 181 (1958) 474]. In principle it is possible by this method to obtain directly the concentration of ions of any given mass number.

The flame, burning at atmospheric pressure, is directed against a very thin window in which there is a small hole of about 0·002 in. diameter. This hole samples about 0·25 cm^3 per second from the flame into a chamber which is evacuated to $\sim 10^{-3}$ mm of mercury by a rapid pumping system. By means of a series of ion lenses, a beam of ions can be directed into the slit of a conventional sector-type mass spectrometer to obtain a mass analysis. Ion concentrations down to 10^7 ions/cm^3 in the flame are readily detectable.

It is found that all the simple ions easily attach one or two, or even to some extent, three water molecules to the parent ion. In hydrogen–air flames, with temperatures $\sim 2\,200°K$, the main ion in the gases above the reaction zone appears to be H_3O^+, and there is probably also H_2O^+. With acetylene–air flames, on sampling the primary reaction zone, ion peaks of varying sizes were found at almost every mass number up to 100, but an analysis has not yet been attempted. In the gases above the reaction zone, the ions are fewer both in number and in type. The peaks observed in hydrogen flames appear also in these, together with peaks which may denote the presence of CH_2O^+ or NO^+. The former is probably ionized formaldehyde rather than hydrated carbon, since no indication of the presence of C was found.

A later communication has been made by the same authors [*Nature, Lond.* 181 (1958) 1261] on investigations of premixed hydrocarbon flames using the same technique as above. The results obtained appear to throw light on the origin of the ions in the reaction zone of such flames, the concentration of these ions being too large to be due to thermal ionization only. For the most part, the ions are those of hydrocarbon molecules and radicals which are evidently formed by very rapid polymerization of the

fuel in the preheating zone of the flame. It is suggested that the formation of solid carbon particles in luminous flames may be due to polymerization of the fuel.

COST OF REMOVAL OF SULPHUR DIOXIDE FROM FLUE GASES

A study of the cost of removing sulphur dioxide from flue gases by existing liquid-scrubbing processes has been made by the Bureau of Mines in cooperation with the Department of Health, Education and Welfare, as a part of the air pollution programme authorized by the Federal Government of the United States. A paper reporting this study has been published by J. H. FIELD, L. M. BRUNN, W. P. HAYNES and H. E. BENSON [*Combustion (int. Combust. Engng Corpn)* 29 (No. 5) (1957) 61].

Three liquid-absorption processes for removing sulphur dioxide from flue gases were chosen, the non-regenerative limestone process, the ammoniacal liquor process, and the regenerative sodium sulphite process. A coal-burning plant of 120 000 kW capacity was chosen for examination. A low-sulphur coal of 1·5 per cent and a high-sulphur one of 5 per cent sulphur were considered. Coal consumption of 1 lb/kWh was used, the hourly coal requirement being 60 tons. The flue gas volume was taken to be 20 million standard ft^3/h with sulphur dioxide concentrations of 0·083 and 0·30 per cent for the low- and high-sulphur coals respectively. Cost estimates were made for removing 90 per cent of the sulphur dioxide from gases of both concentrations and also for 70 per cent removal from the flue gas with the higher concentration of sulphur dioxide.

It is concluded that, in general, the capital requirement for such a power plant would be increased by 10 to 20 per cent by the addition of scrubbing facilities. The operating costs per ton of coal used vary from about $1.25 to 2.00, allowing credit for products, and the costs would be appreciably higher for the ammonia and sodium sulphite processes, with no by-product credit allowed. This amounts to operating costs from 0·6 to over 1 mill per kWh of energy generated, without charge on the capital investment. Actually the cost of coal consumed to generate power amounts to only 2 to 3 mills per kWh, with coal costing from $4.00 to 6.00 per ton.

THERMOACOUSTIC OSCILLATION

Two apparently new types of flame-excited oscillation in a tube have been observed by J. J. BAILEY, of the Shell Development Company, Houston, Texas, in research conducted under the sponsorship of the Office of Ordnance Research, U.S. Army [*J. appl. Mech.* 24 (1957) 333]. One of these types of oscillation occurs with cellular flames and the other with flat flames. They were investigated in the burning of propane–air mixtures in a tube which was effectively open-ended, containing a screen flameholder.

The type of oscillation occurring with a flat flame is described in some detail. The driving mechanism proposed depends on a flame speed that is a function of position, as well as of mixture strength. The resultant instability is found to be in accordance with Rayleigh's criterion [*Nature, Lond.* 18 (1878) 319]. According to this, thermoacoustic systems are

unstable to small periodic disturbances if the fluctuating heat input is at a position such that it has a component in phase with the pressure fluctuations. A procedure is demonstrated by which it is possible to select from all the modes of oscillation which are driven by the action of the flame, that mode to which the system is least stable. The 'least stable' frequency is always one such that the flame is positioned with the second quarter wavelength from the downstream end of the tube. The predictions of a linear, one-dimensional theory which is presented are in good agreement with the experimental results.

SAMPLING OF FLAME GASES

The study of high temperature combustion in the field of jet propulsion necessitates the determination of the state of the combustion gases in and near the region of chemical reaction. For this the composition of the flame gases, amongst other quantities, is required for the small volume of the engine from which the sample is drawn. Chemical analysis of the flame gases will be of value only if the composition of the sample remains unchanged. The preservation of the composition of the gas at the point of sampling presents a serious problem and an important investigation has recently been described by C. HALPERN and F. W. RUEGG, which had for its objective the determination of the effectiveness in this respect of sampling of hot combustion gases by means of water-cooled probes. The work was sponsored by the Power Plants Division, Bureau of Aeronautics, Department of the Navy, U.S.A. [*J. Res. nat. Bur. Stand.* 60 (1958) 29].

Exhaust gas was provided by burning mixtures of methane, air and oxygen in bunsen cones at the discharge port of a nozzle. Water-cooled probes of internal diameter 0·027 to 0·070 cm were used and the effect of conditions of sampling on concentrations of carbon monoxide, carbon dioxide, hydrogen and water vapour was the primary interest of the work. It was found that the probes were unable to quench reactions completely and were unable to preserve the original composition of the gas, but small probes were more effective than large ones. Apparent quenched temperatures derived from the observed compositions were found to be 500° lower than the flame temperatures at 3 050°K. At 2 250°K the difference is small and composition of the gas sample is close to that of the flame gas.

Rate of sampling exerts little influence on the composition of samples, provided there are no fixed gradients of temperature and composition near the sampling point. Probe material and configuration had little effect on sample composition.

HEATS OF COMBUSTION OF AIRCRAFT FUELS

The standard for fuels for use in the Services are becoming more exacting and one of the specifications stipulated for aircraft fuels is a highly accurate value for the net heat of combustion. The experimental determination of reliable values requires considerable skill, and the somewhat expensive apparatus necessary is not always available. Consequently a convenient means of estimating the heat of combustion has been sought by the National Bureau of Standards. Investigations carried out by G. T. ARMSTRONG,

R. S. JESSUP and T. W. MEARS on the relationships between the net he of combustion and other more easily measured properties of aircraft fue have led to a convenient and reliable method for estimating the net heat combustion by means of an empirical equation [*Tech. News Bull. U.S. Bu Stand.* 41 (1957) 151].

Approximate linear relationships exist between the measured heat combustion of a well defined class of fuels and several properties, but th most accurate means of estimation was found to be a method based o the composition of the fuel in terms of hydrocarbon types. The aircra fuels were first analysed by a standard ASTM procedure of silica ge adsorption into saturates, olefins and aromatics. The saturate fractions were further analysed for paraffins and naphthenes. Measured heats of combustion were then fitted by the method of least squares to a linear combination of the weight percentages of paraffins (*P*), naphthenes (*N*), olefins (*O*), and aromatics (*Ar*). The equation is

$$Q_p\,(\text{net})\ \text{B.Th.U./lb} = 190{\cdot}892\,P + 188{\cdot}80\,N + 176{\cdot}73\,O + 172{\cdot}65\,Ar$$

FLAME RESEARCHES AT IMPERIAL COLLEGE, LONDON

Two papers have recently been published by F. J. WEINBERG, of the Department of Chemical Engineering, Imperial College, London, one dealing with the calculation of equilibrium gas compositions at high temperatures and the other with optical considerations in defining the thickness of laminar flames in premixed reactants [*Proc. Roy. Soc. A* 241 (1957) 132; *A* 243 (1957) 107].

The first of these papers deals with the difficulty of solving the considerable number of non-linear simultaneous equations necessary for determining equilibrium gas compositions at high temperatures in calculations of flame temperatures. Two of the most common practical cases are examined, the C + H + O and the C + H + O + N systems without carbon deposition. For solution by successive approximations, it is shown how explicit equations can be derived for the calculation of errors in terms of the assumptions. Such equations need be derived only once for each set of elements and apply irrespective of temperature, pressure, fuel and oxidant type and do not have to be altered at each approximation.

In the second of the papers the concept of flame thickness and the necessary criteria for its definition and measurement are discussed. Ra deflections due to refractive index variations across a flame result in th apparent thicknesses of luminous zones being always in part optical illusion Expressions in terms of burning velocity, flame geometry and physic properties of the reactants are derived for the apparent thickness of a idealized luminous zone of no real thickness and numerical values ar deduced for typical flames used in combustion research. These calculate values are sufficiently similar to measured values to lead to the conclusio that, at normal pressures, such measurements do not as a rule give a tru measure of flame thickness. In the later part of the paper, the examinatio of flames by optical methods using extraneous light is discussed. Satis factory simple ray deflection methods are indicated which can be used t measure flame thickness according to various definitions.

PRESSURES IN GASEOUS DETONATION WAVES

During the past few years investigations by G. B. KISTIAKOWSKY *et al.* have shown that the velocities of plane detonation waves in the steady state in gaseous mixtures contained in straight tubes are influenced by the energy losses to the walls of the tube [*J. Amer. chem. Soc.* 72 (1950) 1080; *Second Office of Naval Research Symposium on Detonation, Washington*, p 80, 1955]. For tubes the diameters of which are less than 10 cm, the velocities are found to decrease with decreasing diameter. To examine this further, D. H. EDWARDS and G. T. WILLIAMS, of the University College of Wales, Aberystwyth, have studied the influence of tube diameter on the pressure/time relationships of the waves, using tubes 10 ft long and of 10, 3·8 and 1·6 cm diameter, since the effect in this case is likely to be more pronounced than in the case of velocity [*Nature, Lond.* 180 (1957) 1117]. The static pressure/time curves for the mixture $2H_2 + O_2$ were examined in detail for the tubes of different diameters. The general features of these curves show an effect of tube diameter on the pressures, and the periods of pressure oscillations agree closely with the times of traverse of a sound wave in the hot gases behind the detonation front, across the respective tube diameter. This observation lends support to the hypothesis that energy is abstracted from the detonation wave through the formation of rarefaction waves at the wall of the tube. Such waves, travelling inwards with acoustic velocity, would cause a lowering of temperature and rate of chemical reaction.

ABSORPTION SPECTRA OF FLAMES

G. N. SPOKES and A. G. GAYDON, of the Imperial College of Science and Technology, have recently described their work towards solving the problem of detecting absorption bands of intermediate oxidation or pyrolysis products in premixed flames [*Nature, Lond.* 180 (1957) 1114]. They have used flat, near-limit flames, of the type developed by Sir ALFRED EGERTON and J. POWLING [*Proc. Roy. Soc. A* 193 (1948) 1720], together with a very bright xenon high-pressure lamp as background source, and a system of mirrors to reflect the beam of light backwards and forwards a number of times through the flame gases.

With this multiple-reflection technique and a medium quartz spectrograph, diethyl ether–air flames showed strong absorption bands of formaldehyde, which are strongest in the region between the cool and main flames. Under carbon-forming conditions benzene absorption bands were also found, and these bands were found much more clearly in hexane–air flames. It is suggested that the new observation of benzene may support a theory of ring closure as a stage in carbon formation, rather than one depending on the breakdown of acetylene to carbon. The presence of benzene and weakness of formaldehyde in hexane–air flames may indicate that, in premixed flames of hydrocarbons, the formation of pyrolysis products is more rapid than that of partial oxidation products.

VORTEX-TUBE COMBUSTION CHAMBER

A new burner based on the vortex tube of G. J. RANQUE [*J. Phys. Radium* 4 (1933) 324] has been described in a communication by J. M. F. VICKERS,

of the University of Nebraska [*Nature, Lond.* 180 (1957) 1271]. The burner, made of steel, consists of a standard vortex tube of the type described by Ranque, with a range of orifices to restrict the flow of gas in one direction. Rates of flow are obtained with this apparatus which could not be obtained in the earlier work by N. P. W. MOORE and D. A. MARTIN [*Fuel, Lond.* 32 (1953) 393] who used a single-outlet vortex tube made of Pyrex glass and recorded the peculiar behaviour of premixed propane–air flames. In experiments carried out by Vickers two further forms of combustion are found to exist. The vortex-tube technique described in this communication appears to be a useful compact combustion chamber and a possible research tool for the investigation of cool flames.

AN EQUATION FOR BURNING VELOCITY

A conference on *Flame Reactions and Explosions*, organized by the Deutschen Bunsen-Gesellschaft für physikalische Chemie e.V. was held in Troisdorf from 18 to 20 October 1956. Twenty papers were presented, thirteen of them dealing with gaseous combustion, and the remainder mostly with solid explosives. These papers have been issued as a report occupying the whole of one issue of *Zeitschrift für Elektrochemie* [61 (1957) 557 to 692].

In a paper read to the conference by A. VAN TIGGELEN, J. PONCELET and P. J. SLOOTMAEKERS, some ideas on chain branching and flame propagation that they had put forward briefly at the Sixth International Symposium on Combustion, in August 1956 [*Sixth Symposium (International) on Combustion, Yale University, 1956*, p 61. Reinhold: New York, 1957], are elaborated and an equation is proposed for the burning velocities of various fuel mixtures [*Z. Elektrochem.* 61 (1957) 579].

In the theory of flame propagation developed there are two fundamental ideas. These are: (*i*) the diffusion of chain-propagating fragments from the flame front into fresh gas, and (*ii*) the activation energy for chain branching. On this basis an expression is developed for burning velocities applicable to mixtures of various fuels with oxygen over a wide range of compositions. The equation proposed has the form

$$V_0 = K\,[f(\%)\,.\,\exp(-E/RT)]^{1/2}$$

where V_0 is the burning velocity for the cold gases, K is a function of the physical parameters, $f(\%)$ is a kinetic expression and is a function of the mixture composition, and E is an apparent activation energy.

It is pointed out by the authors of this theory that it has nothing in common with that proposed a few years ago by C. TANFORD and R. N. PEASE [*J. chem. Phys.* 15 (1947) 431, 433 and 861]. In particular no radical concentration appears in the final formula for burning velocity. In fact, the chain-carrier concentration at any point of the flame front is assumed to be entirely dependent on the branched chain kinetics and is not in any way connected with the equilibrium concentration in the burnt gases.

COMBUSTION OF LIQUID FUEL SPRAYS

An important contribution towards elucidating the general problem of the mechanism of combustion of liquid fuel sprays has been made by M. A. Saad by an investigation of the evaporation and combustion of single fuel droplets in a hot atmosphere [*Microfilm (Dissert.) Abstr.* 17 (1957) 1298; *Publ. No. 21 355*, 137 pp. University Microfilms: Ann Arbor, Mich.].

The experimental procedure consisted of allowing single fuel droplets to fall freely in a vertical furnace. After leaving a fuel dropper, the droplets accelerated to about 87 per cent of their terminal velocity by the time the first photographing stage was reached. Each droplet was photographed at several positions as it fell, and a record of droplet diameter and elapsed time was obtained. At every photographing stage, the droplet was detected by a multiplier phototube which actuated a high speed photolight. The fuel droplets fell in the furnace under gravity, buoyancy, and drag forces. They were burned in hot air while exposed to thermal radiation from the furnace walls. Reynolds number was not a controllable factor because the droplets changed in both diameters and velocities during their fall. Kerosine and two pure hydrocarbon fuels, *n*-heptane and *iso*octane, were investigated at a furnace temperature of 820°C. The range of droplet diameters was approximately 1 150 to 300 microns. The combustion of the fuels investigated depended on the properties of the fuel, droplet size, and the relative velocity between the droplet and the furnace atmosphere, other factors such as ambient temperature and furnace atmosphere being unchanged. Preheating of the droplet was mainly by conduction and convection from the ambient atmosphere, since radiation from the furnace walls was found to have a comparatively small effect. Heat transfer to the interior of the droplet modified the rate of vaporization since an appreciable portion of the heat transferred was used for the internal heating of the droplet. During combustion, heat was transferred to the droplet from the local flame produced by the combustion of the vaporized fuel around and in the wake of the droplet. The change of droplet size of the fuels investigated was represented by the equation

$$D^2 = D_0^2 - Ct$$

where D is the diameter of the droplet at time t, D_0 is the initial diameter of the droplet and C is the coefficient of combustion. C was found to depend on the nature of the fuel and the velocity of the falling droplet. For the fuels investigated C varied from 0·02 to 0·025 cm²/s. Results show that the presence of the flame decreased the drag of the falling droplet.

XXXIST INTERNATIONAL CONGRESS OF INDUSTRIAL CHEMISTRY

The thirty first International Congress of Industrial Chemistry, organized jointly with the Federation of Chemical Industries of Belgium, will take place in Liège, Belgium, during 7 to 20 September 1958, it is announced by the Société de Chimie Industrielle of Paris.

Ten groups of subjects comprising some thirty separate sections are envisaged and of these Group II covers the following: Section 7—Solid and gaseous combustibles; Section 8—Liquid combustibles and petroleum products; Section 9—Petrochemistry. In addition it should be noted that Section 18 (Group VII) is concerned with powders and explosives (*Chairman*—P. L. GÉRARD).

All correspondence in connection with this Congress should be addressed in the first instance to the Sécrétariat général, 32 rue Joseph II, Bruxelles IV, or, during the period 6 to 12 September 1958, to the Palais des Congrès, Jardin d'Acclimatation, Liège.

COAL AND COKE FUMES

It is often said by users of coke for domestic heating that it gives more 'fumes' than coal and for that reason it is not always a popular fuel. This has now been investigated at the Fuel Research Station by determining the emission of oxides of sulphur and other undesirable constituents from an openable stove (*The Investigation of Atmospheric Pollution, 29th Report*. Department of Scientific and Industrial Research: H.M.S.O., London, 1958).

It was found that, under the particular conditions used, the sulphur is emitted more rapidly from coal than coke, giving a higher maximum concentration of oxides of sulphur in the flue gas, but that for equal weights of fuel burnt the proportions of sulphur emitted from coal and coke are similar. Analysis for harmful constituents did not provide any evidence for the idea that more 'fumes' are emitted from coke than coal, but it is considered that the idea may nevertheless have some basis. It is pointed out that a downdraught is most likely to occur just after a domestic fire has been lit, when the chimney is cold. At this period a coal fire is actually emitting more harmful gases than a coke fire. With a coal fire at this stage, however, the characteristic smell of oxides of sulphur is masked by smoke, whereas with a coke fire it is readily noticed since there is no smoke.

SCIENCE IN THE USE OF COAL

A three-day residential Conference on 'Science in the Use of Coal', organized by the Institute of Fuel was held in the University of Sheffield from 15 to 17 April 1958. There were five sessions for the presentation of papers dealing with: (*i*) physics and chemistry of coal, (*ii*) preparation and breakage, (*iii*) carbonization, (*iv*) combustion and gasification, (*v*) reactivity of cokes and chars.

In the session on combustion and gasification an introductory survey was given by R. H. ESSENHIGH and M. G. PERRY and six other papers were communicated. Three of these papers are referred to in notes which follow this. In the session on reactivity of cokes and chars H. E. BLAYDEN gave an introductory survey and four papers were presented.

A final report of the conference, comprising the full text of the seven introductory surveys and thirty six papers, together with discussion, is to be published by The Institute of Fuel, price £2 10s. 0d.

ABATEMENT OF SMOKE FROM METALLURGICAL FURNACES

Work in the programme of the Fuel Research Board on the abatement of atmospheric pollution has been continued in the University of Sheffield under the supervision of Professor M. W. THRING on the problem of heat-treating steels satisfactorily and economically without producing smoke (*The Investigation of Atmospheric Pollution, 29th Report*. Department of Scientific and Industrial Research: H.M.S.O., London, 1958). It had already been shown that a furnace atmosphere could be maintained so that although little smoke was produced the quality of the steel was unimpaired. More recently the problem of obtaining an even distribution of temperature in the furnace without making smoke has been examined. With furnaces of unsuitable design the method in the past has been to use a *long flame* coal with deficiency of air to obtain a long luminous flame, and then to attempt to burn the soot afterwards. At temperatures below 800°C this is not easy and research on the rate of burning of such soot has been undertaken. An account of this work has been presented by G. UNDERWOOD and M. W. THRING to the Conference on 'Science in the Use of Coal' (see above). In this work a constant flow of smoke was produced by pulling a tray of coal across one section of an electrically heated furnace which consisted of several sections of 2 in. diameter stainless steel tube erected vertically. The smoke was burned with preheated air, injected with high velocity through twelve radial jets, and the unburned smoke was estimated by filtration through a water-cooled porous stainless steel filter. The smoke was found to burn in preference to methane and unsaturated hydrocarbons, and at an air–smoke temperature of 750°C, about 90 per cent of the smoke can be burned in less than 0·5 sec, using about 60 per cent of the air theoretically necessary to burn all the volatiles evolved. Consequently it can be stated that there need be no smoke problem in heat treatment furnaces if there is good mixing between hot secondary air and the smoke, and the air and smoke are allowed sufficient time to react, provided the smoke has not been heated to a much higher temperature before the pre-heated air is admitted to the combustion chamber.

BURNING VELOCITY OF COAL-IN-AIR SUSPENSIONS

Considerable research has been made in the past few years by the Safety in Mines Research Establishment on the control of coal dust explosions by spreading salt on coal dust deposits, followed by periodical moistening. The depositing dust is entrapped by the crystallizing salt during the drying process and becomes resistant to dispersion by an advancing explosion wave. There is an additional effect, however, in that sodium chloride in suspended particle form has a suppressing effect on coal dust–air flames. The mechanism of this suppressing action is now being investigated by J. H. BURGOYNE and V. D. LONG, in the Department of Chemical Engineering, Imperial College of Science and Technology, London, and they presented a paper on measurements of the burning velocity of small coal dust–air flames, to the Conference on 'Science in the Use of Coal' (see above).

Measurements were made of the burning velocity under laminar conditions on downward pointing burners of § in. i.d. The investigated concentration

range was from 80 to 300 mg/l., which extends from the stoichiometric concentration for the whole coal to the stoichiometric concentration for the volatiles. Size fractions with mean mass sizes from 11 to 120 microns were burnt. It was found that the burning velocity increases with concentration until this reaches about twice the stoichiometric concentration for the whole coal and thereafter remains constant. With increasing particle size and salt addition, the burning velocity is lowered.

An outstanding feature of the results is the very low magnitude of burning velocity in comparison with the flame speed measurements of J. TAFFANEL and A. DURR [*Ann. Min., Paris*, Ser. 11, 2 (1912) 167] which were until fairly recently the only published results of this kind. A possible explanation of the large difference between the present values of burning velocity and the high values of flame speed measured by Taffanel is that the flames studied by the latter were turbulent. If so, the effective flame surface would be considerably greater, due to the broken flame front, than that in the laminar conditions of the present experiments. It is suggested by the authors of the paper that for the turbulent conditions the values of the flame speed may be 50 to 200 times the burning velocity, as compared with 1 to 5 times the burning velocity for laminar conditions.

RADIATION FROM LUMINOUS FLAMES

J. W. HARDCASTLE and M. W. THRING, University of Sheffield, communicated a paper to the Conference on 'Science in the Use of Coal' (see above) describing experiments to determine the effect of varying the combustion conditions on the radiation characteristics of flames over a coal bed fed continuously from the top. The object of the work was to derive empirical formulae whereby to predict variations in the radiation characteristics of flames along their lengths. Knowledge of these characteristics is essential for furnace and boiler combustion-chamber design in order to make satisfactory use of heat transfer by radiation.

A semi-industrial scale combustion chamber was built and fired by a sprinkler stoker of the rotary feed type. The secondary air was injected by a system of radially positioned jets, so as to give very rapid mixing. The Schmidt method was used in the radiation measurements for determining flame emissivity and temperature, using two narrow-angle total-radiation pyrometers. Rate of coal feed, percentage secondary air and secondary air injection velocity were varied, and a statistical method was used to assess the significant effects on the dependent variables, flame emissivity, temperature and radiation to a cold sink.

It was found that the radial injection of secondary air at a high velocity was very efficient in promoting good mixing of the air and gases leaving the fuel bed, so that very low values, down to 5 per cent, of secondary air had to be used in order to obtain luminous flames, even though the overfeed method of firing was favourable to the production of flames containing a high concentration of soot. A critical temperature has been postulated, estimated for the present mixing efficiencies as approximately 1 600°F. For temperatures above the critical value, the combustion of soot particles is regarded as being controlled by the physical conditions, and below the

critical value by both the physical and chemical conditions. A design curve has been put forward relating the variation of the overall coefficient of absorptivity along the flame length for known combustion conditions similar to those used in the research.

ULTRA-HIGH TEMPERATURES

A study of methods for obtaining ultra-high temperatures has been made by A. V. GROSSE and A. D. KIRSHENBAUM, of the Temple University Research Institute, Philadelphia [*PB121074*; Dec. 1955, 41 pp; abstr. in *U.S. Govt Res. Rep. 27* (12 April 1957) 172]. Carbon subnitride, or dicyano acetylene, C_4N_2, was burnt with oxygen or ozone to carbon monoxide and nitrogen. A temperature of approximately 5 260°K has been reached and this is said to be the highest continuous temperature attained so far by chemical means.

DIFFUSION COMBUSTION OF LIQUIDS

A paper by V. I. BLINOV and G. N. KHUDYAKOV describes a study of the changes in combustion which occur with different areas of exposed surfaces of gasoline, kerosine, diesel oil and other petroleum fractions. Circular containers and tanks of diameters from 0·5 cm to 260 cm were used [*Dokl. Akad. Nauk SSSR* 113 (1957) 1094].

Changes in the appearance of the flames were noted. In a container of 1 cm diameter there was a flame with a steady conical shape. With a slightly larger diameter, pulsations occurred, reaching a maximum frequency of 18 to 20 per second; with a further increase in diameter the pulsations diminished. With a container of 3 cm diameter the upper part of the flame became unstable and the region of instability moved down with increasing diameter until at 15 cm the whole of the flame was unsteady.

Three types of relationship were found between the rate of combustion and the container diameter. The rate of combustion was measured by the rate of fall of the fuel surface in the container. The rate of combustion was found: (*i*) to decrease at first with increase in diameter, (*ii*) to increase with increase in diameter above 10 cm, (*iii*) to remain practically constant for diameters above about 1 m.

The Reynolds numbers associated with the flow of fuel vapour were determined approximately. It was found that in type *i* above the conditions of flow were laminar, in type *iii* turbulent, and in type *ii* both laminar and turbulent flow.

OXIDATION OF HYDROCARBONS

N. N. SEMENOV, Director of the Institute of Physical Chemistry of the Academy of Sciences, U.S.S.R., has recently put forward some views on the mechanism of the oxidation of simple hydrocarbons [*Chim. et Industr.* 79 (1958) 3]. From studies under his direction, by N. V. FOK and A. B. NALBANDJAN, on methane, ethane and propane, Semenov concludes that at low temperature hydroperoxides, the only products of reaction, are formed by a photochemical reaction. As the temperature is raised aldehydes are found in the products of reaction and appear, like the

hydroperoxides, to be primary products. The more the temperature is raised the more is the formation of peroxides inhibited and the proportion of aldehydes increased, until peroxides are no longer present. This is attributed to the peroxide radical being able to exist in isomeric forms, one form decomposing at higher temperatures into aldehyde and hydroxyl radical. With the higher hydrocarbons, the peroxide radicals may undergo isomerization in two different ways, giving numerous intermediate products.

With regard to the mechanism of chain initiation in the thermal oxidation of hydrocarbons, Semenov points out that the spontaneous dissociation of the initial molecules into primary radicals, which is commonly believed to take place, is not possible with simple hydrocarbons because the energy required for the scission of a C—C bond, more than 80 kcal, would not be available at the usual temperatures of oxidation of hydrocarbons. The interaction of two radicals, however, is often accompanied by a disproportionating process and practically occurs without the barrier of activation being involved, that is, at almost every collision. For example

$$\dot{C}_2H_5 + \dot{C}_2H_5 \longrightarrow C_2H_4 + C_2H_6 + 60\,\text{kcal}$$

then the formation of two free radicals in the reaction between two molecules

$$C_2H_4 + C_2H_6 \longrightarrow 2\dot{C}_2H_5$$

will take place with an activation energy equal to the energy consumed in the above process. In a similar way the formation of free radicals may be supposed to take place in reactions between hydrocarbons and oxygen. In this connection it is noted that active centres are created very efficiently by the walls of the experimental vessel.

ACS GAS AND FUEL CHEMISTRY MEETING

A special spring meeting of the Gas and Fuel Chemistry Division of the American Chemical Society was held from 15 to 16 May 1958 at the Illinois State Geological Survey, Urbana, Ill. Eleven papers were presented to the meeting and seven of these relate to the combustion of gaseous and liquid fuels. These latter deal with: the composition dependence of the burning velocity of lean hydrocarbon flames; effect of initial temperature on the flashback of laminar and turbulent burner flames; performance coefficients and flame stability of gas appliance burners; quenching of flames and flashback on shut-off with gas appliance burners; smoke limits of bunsen burner ethylene–air flames; chemical reactions in diffusion flames; radiation from jet combustor flames.

SEVENTH INTERNATIONAL SYMPOSIUM ON COMBUSTION, 1958 LONDON AND OXFORD

Readers of *Combustion and Flame* may like to be reminded that the Seventh International Symposium on Combustion will take place in London and Oxford (England) from 27 August to 3 September. The theme of the

Symposium will be 'The Physics and Chemistry of Flames'. Full information may be obtained from the Chairman, The Combustion Institute Committee, c/o The Institute of Fuel, 18 Devonshire Street, Portland Place, London, W.1.

W. A. KIRKBY

FUEL

Readers of *Combustion and Flame* may like to know that the following *Notes* were published in the April issue of *Fuel*:

Sulphur removal from flue gas

Natural gas as town gas in Scotland and North Wales

Investigation of atmospheric pollution

Town gas from methanol

Publication

GAZEIFICATION ET OXYDATION DES COMBUSTIBLES

J. MEUNIER. Paris: Masson, 1957. 494 *pp.*

THE book is divided into four sections. The first section of 30 pages serves as an introduction, in which the scope of the work is defined as including all the processes by which fuels of any kind are converted by the action of free or combined oxygen into combustible gaseous products. These gaseous products may then be used as fuel or as raw material for chemical conversion.

The second section, of 71 pages, is devoted mainly to the constitution and properties of solid fuels. The third section of 178 pages, on the theoretical bases of the subject, deals with stoichiometry, thermochemistry, thermodynamics, kinetics and general theory. Economics are not considered in detail.

The fourth section, 214 pages, deals with the technology of the actual processes, including conventional producers and more recent processes such as the Lurgi, Winkler, Onia–Gegi and many others. The processes are described in order, grouped according to the method of supplying heat and whether they are carried out in a fixed bed, a fluidized bed, or in suspension.

The last section seems the most valuable part of the book. The order of presentation is logical and the descriptions are very clear and well illustrated. The principles of the various processes, their similarities and differences and their relative advantages are well brought out. An up-to-date bibliography of 351 references and satisfactory indices help the reader to obtain information about any particular process. The inclusion of the earlier sections undoubtedly makes the book more complete and more convenient to use, but it must add to the cost, and some of the material, especially that in the second section, is quite easily obtainable elsewhere.

On the whole, the book is an excellent survey, and greatly facilitates the task of keeping up with developments in its field. An English edition would be welcome.

M. J. G. WILSON

Letters to the Editors

Letters to the Editors on points of scientific interest related to combustion and flames are invited. The Editors do not hold themselves responsible for opinions expressed in correspondence. Anonymous contributions cannot be accepted.

Laminar Flame Theory

S. S. PENNER[1] has pointed out two errors in a recent paper by one of the writers[2]. The first is that equation 62 of J. CORNER'S approximate method[3] should read $g=\tau^{n+1}$, whereas the corresponding assumption of the Adams method[4] should read $g=\tau^{n}$. These two expressions were interchanged in the printed version due to a clerical error. The expressions for the eigenvalues, and the conclusions about the relative merits of the theories, are unaffected by this amendment.

The second error concerns the attribution to K. A. WILDE[5] of the approximate procedure for solving the flame equations in which g is taken as of the form τ^{1+a}, where a is chosen to satisfy the differential equation at the hot boundary. Closer examination of Wilde's paper shows that he did not choose the exponent in this way, but in a way that amounts to his carrying out the Corner second approximation.

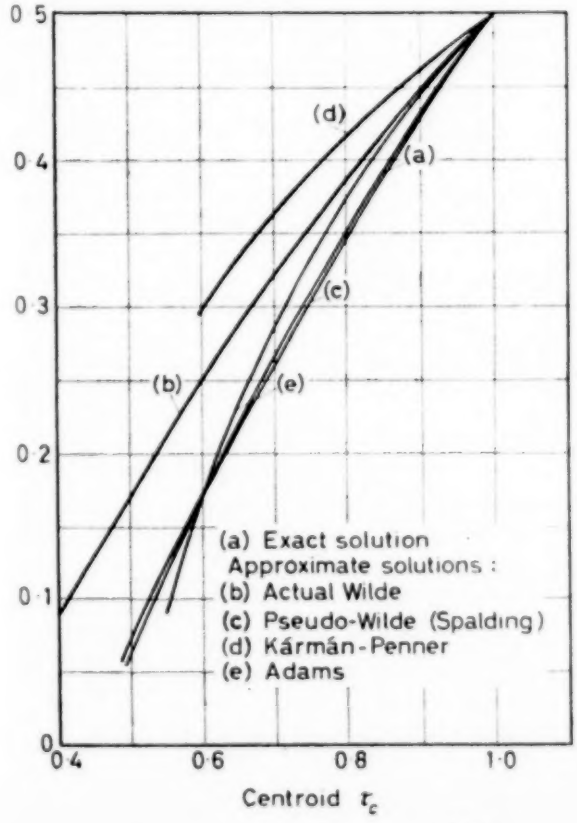

Figure 1. Eigenvalues, λ, versus centroid position, τ_c, of reaction rate curve, for reactions belonging to family $(\phi=(n+1)(n+2)(1-\tau)\tau^n)$ where n is a parameter

Figure 1 shows that Wilde's actual procedure gives less accurate eigenvalues than does the procedure attributed to him (marked 'pseudo-Wilde') which in fact gives results in close agreement with the exact ones. The new approximate procedure may be regarded as a refinement of the von Kármán–Penner procedure[6], for the two procedures use the same criterion for $dg/d\tau$ at the hot boundary, but the new one uses a 'smoother' profile ($g=\tau^{a+1}$) than that of von Kármán–Penner (two straight lines).

The approximate results for non-normal diffusion reported in ref. 2 should now be regarded as based on an extension of the pseudo-Wilde theory rather than on an extension of Wilde's actual procedure.

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Semi-empirical Determination of Gas Characteristics in the Chapman–Jouguet State

(*1*) In a recent paper[1], using the classical hydrodynamic theory[2] of detonation waves but without employing an equation of state for burnt gases, we developed a relation between: (*i*) the specific volume v_b of the burnt gases in the Chapman–Jouguet state; (*ii*) the velocity D of the detonation wave; (*iii*) two partial derivatives of this velocity versus two of the state variables (temperature T_f, specific volume v_f, pressure p_f) of the fresh explosive; (*iv*) the following physical properties of this explosive: the specific heat ratio γ_f, the thermal expansion $\alpha_f = v_f^{-1}(\partial v_f/\partial T_f)_{pf}$ and the sound velocity a_f.

Some results are outlined here of a first application of this relation to the explosives which can be assimilated to a mixture of perfect gases ($p_f v_f = n_f R T_f$).

(*2*) For such explosives the above mentioned relation is

$$\sigma^2 - 2K\sigma - L = 0 \qquad \ldots . [1]$$

where

$$\sigma = v_f (v_f - v_b)^{-1}; \qquad M = D a_f^{-1} \qquad \ldots . [2]$$

$$l = (\partial \log D / \partial \log T_f)_{p_f} \quad ; \quad n = (\partial \log D / \partial \log p_f)_{T_f} \qquad \ldots . [3]$$

$$\left.\begin{aligned} K &= \frac{\gamma_f M^2 [2 + (\gamma_f + 1) n + (\gamma_f - 1) l]}{2\gamma_f M^2 - \gamma_f - 1} \\ L &= \frac{2\gamma_f (\gamma_f - 1) M^2 [1 + (n + l) \gamma_f M^2 - l]}{2\gamma_f M^2 - \gamma_f - 1} \end{aligned}\right\} \qquad \ldots . [4]$$

and in which only the positive root σ' corresponding to $\mu = v_f v_b^{-1} > 1$ is to be taken into account.

If for a given explosive we know $D(T_f, p_f)$ (D function of initial conditions specified by T_f and p_f), we can deduce the values of l and n, and since the other parameters (v_f, γ_f, a_f) are known, equation 1 will facilitate computation of the specific volume v_b. With that we can now deduce from the relations of the hydrodynamic theory the pressure p_b, the sound velocity $a = D\mu^{-1}$, the velocity $u_b = D - a_b$ and the isentropic expansion coefficient $\Gamma_b = (\partial H_b / \partial E_b)_{s_b} = \partial_b^2 (p_b v_b)^{-1}$. The ratio $n_b T_b / n_f T_f$ may be also computed but only if we assume that $p_b v_b = n_b R T_b$.

(*3*) Inspection of equation 4 giving K and L shows that of the two partial derivatives l and n, only the second has to be known accurately. This is particularly interesting since accurate measurements of the variations of D versus p_f for a given temperature T_f are easier than those of D versus T_f for a given pressure p_f. It can also be seen that according to the order of magnitude and the signs of different parameters (particularly: $n \sim -l \sim 10^{-3}$ to 10^{-1}), μ is about the order of magnitude of $1 + \gamma_f^{-1/2}$. Again, as $\mu \fallingdotseq 1 + \Gamma_b^{-1}$, in a first and very rough approximation: $\Gamma_b \fallingdotseq \gamma_f^{1/2}$. The practical interest of these remarks is, however, small, the orders of magnitude of μ and Γ_b being now well known, but the use of the equation 1 without any simplification gives some new possibilities.

(*4*) In order to point out these possibilities we have computed the characteristics of the Chapman–Jouguet state for the $H_2 + 0{\cdot}5\,O_2$ mixture at $p_f = 1$ atm and $T_f = 283°K$. The l and n values have been obtained using H. B. DIXON'S[3] data for $D(T_f, p_f)$. The computation of n has been done with good accuracy, $\log D$ being, in the 0·4 to 2·0 atm range for $T_f = 283°K$, practically a linear function of p_f. But it has not been possible for l: the only data known being $D = 2\,821$ m/s for $T_f = 283°$ and $D = 2\,790$ m/s for $T_f = 373°K$ at $p_f = 1$ atm.

Our results and those got from thermodynamic data by B. LEWIS and J. B. FRIAUF[4] and by G. B. KISTIAKOWSKY, D. J. BERETS and F. GREENE[5] that we have completed by a computation of μ, a_b, u_b, Γ_b, and $n_b T_b / n_f T_f$) summarized in the table below, corroborate the main conclusions of these authors. Moreover, they show that equation 1 will allow control of the data used in the *a priori* computation of characteristics of a detonation wave, by a comparison of not only the velocities of the wave, but also of the values of the other Chapman–Jouguet state characteristics.

(5) An account of the application of the method described here to condensed explosives will be given in another paper[6].

Table 1

D m/s	μ	p_b atm	a_b m/s	u_b m/s	Γ_b	n_bT_b/n_fT_f	*Computed*
2821*	1·78	18·70	1585	1236	1·220	10·50	*here*† $T_f=283°K$
2806	1·78	18·05	1575	1231	1·224	10·13	*by* (4) $T_f=291°K$
2852	1·72	18·06	1655	1197	1·250	10·49	*by* (5) $T_f=298°K$

*Observed, see ref. 3. †With $l=-0·04$ and $n=+0·0365$.

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